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Ionic Liquid Technology in Metal Refining: Dissolution of Metal Oxides and Separation by Solvent Extraction

Sil WELLENS

Dissertation presented in partial fulfillment of the requirements for the degree of Doctor in Science

19 February 2014

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ABSTRACT

Ionic liquids form a relatively new class of solvents entirely composed by ions that have specific properties such as low volatility, low flammability, large electrochemical window, broad liquidus range and a high thermal stability. These properties make ionic liquids very attractive for applications in a wide variety of fields. In the field of metal processing, ionic liquids have been used as extraction media in solvent extraction and promising results have already been reported. Nevertheless, there are some challenges for the use of ionic liquids as extraction phase. The general application of ionic liquids for liquid-liquid extraction processes is hampered because of the ion exchange problem where metal ions are exchanged with the ionic constitutes of the ionic liquid. This PhD thesis presents different approaches in an attempt to overcome the practical problems with ion exchange and offers a greener approach to solvent extraction by replacing volatile organic compounds with non-volatile ionic liquids. Furthermore, the dissolution of metal oxides in ionic liquids is generally poor and so far there are only a few examples which reports the successful dissolution of metal oxides. In this thesis another approach for the processing of metal oxides in ionic liquids is presented and further, the metal species in solution and the reaction between selected metal oxides and ionic liquids are investigated.

The first part presents the use of the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) as extraction phase for the extraction and separation of metal ions. The selective extraction of cobalt from nickel to Cyphos®IL 101 has been

demonstrated. In the described process no additional organic diluents are added to the ionic liquid phase, which is a main advantage in comparison with the current state as no volatile odorous compounds are emitted offering thus a more sustainable approach to solvent extraction. Furthermore the practical issues accompanied with ion exchange are overruled in this case – the metals are extracted as anionic chloro complexes and because a chloride based ionic liquid is used, there is no net loss of the ionic liquid constitutes to the aqueous phase. The separation between cobalt and nickel shows a very high selectivity with a separation factor of about $5{\cdot}10^4$. The properties of the extraction phase and the extraction parameters are discussed and compared with other phosphonium and ammonium ionic liquids. This batch ionic liquid extraction process has been transformed subsequently into a lab pilot-scale continuous process and the performance of this process proves to be competitive with currently applied industrial processes. This work is a significant step towards achieving a competitive industrial process using ionic liquids as extraction phase.

The ionic nature of ionic liquids make them able to absorb water. In the second part advantage is taken of this behaviour to obtain an water saturated acidic solution of trihexyl(tetradecyl)phosphonium chloride used to dissolve metal oxides (CaO, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO) directly in ionic liquid phase. This presents particular opportunities for bringing metal ions which cannot enter the ionic liquid phase via extraction into ionic liquid solution and it offers opportunities to further process these metals in ionic liquid phase. Additionally, the selective back-extraction to aqueous phase of these dissolved metals is investigated.

In the third part, another approach for the use of ionic liquids in metal separation is applied by which both the aqueous phase and the organic phase are replaced by two mutually immiscible ionic liquids. A proof of principle for the separation of metals by redistribution between two mutually immiscible ionic liquids is given and the process is applied for the cobalt and nickel mixture. In the process cobalt is selectively extracted from 1-ethyl-3-methylimidazolium chloride to trihexyl(tetradecyl)phosphonium bis-[2,4,4-trimethylpentyl]phosphinate. Processing steps such as washing, stripping and regeneration the ionic liquid phase are further discussed.

The last part presents the dissolution of metal oxides in imidazolium ionic liquids. Although ionic liquids show in general a low solubility of metal oxides it is shown that metal oxides can be dissolved in imidazolium ionic liquids. Silver(I) carbene complexes are formed upon reaction of Ag_2O with the imidazolium moieties which have a hydrogen atom in the C2 position. The presence of carbenes in the solution is detected by ^{13}C NMR spectroscopy and the reactions were also monitored by Raman spectroscopy. The dissolution of other metal oxides, namely CuO, ZnO and NiO in imidazolium ionic liquids is studied and it is found that stable zinc(II) carbenes are formed in solution.

NEDERLANDSTALIGE ABSTRACT

Ionische vloeistoffen vormen een relatief nieuwe klasse van solventen die volledig zijn opgebouwd uit ionen en specifieke eigenschappen bezitten zoals een lage dampspanning, niet-ontvlambaarheid, breed elektrochemisch venster, vloeibaar over een breed temperatuursgebied en een hoge thermische stabiliteit. Deze eigenschappen maken ionische vloeistoffen zeer aantrekkelijk voor een waaier aan toepassingen. In het toepassingsdomein van metaalraffinage worden ionische vloeistoffen reeds gebruikt als extractiemedia in solventextractie en zijn er al veelbelovende resultaten behaald. Desondanks, zijn er nog steeds uitdagingen voor het gebruik van ionische vloeistoffen als extractiefase. De toepassing van ionische vloeistoffen in vloeistof-vloeistof extractieprocessen wordt voornamelijk verhinderd door ionuitwisseling waarbij metaalionen uitgewisseld worden met de ionen van de ionische vloeistof. Dit doctoraatsproefschrift stelt verschillende benaderingen voor om het praktische probleem van ionuitwisseling te omzeilen en biedt een milieuvriendelijkere aanpak aan solventextractie door vluchtige organische verbindingen te vervangen door niet-vluchtige ionische vloeistoffen. Daarnaast lossen metaaloxiden over het algemeen niet goed op in ionische vloeistoffen. Tot nu toe zijn er slechts enkele voorbeelden gerapporteerd die de oplosbaarheid van metaaloxiden aantonen. In dit doctoraatsproefschrift wordt een

andere aanpak aan voor het oplossen van metaaloxiden voorgesteld en verder wordt de reactie tussen geselecteerde metaaloxiden en ionische vloeistoffen onderzocht.

Het eerste gedeelte beschrijft het gebruik van de ionische vloeistof trihexyl-(tetradecyl)fosfoniumchloride (Cyphos® IL 101) als extractiefase voor de extractie van metaalionen. De selectieve extractie van kobalt naar Cyphos® IL 101 wordt voorgesteld, waarbij nikkel in de waterfase achterblijft. In het beschreven proces zijn geen organische solventen toegevoegd aan de ionische vloeistoffase wat een groot voordeel is in vergelijking met huidige processen omdat er geen vluchtige en kwalijk riekende verbindingen verdampen wat resulteert in een duurzamere aanpak voor solventextractie. Ook biedt dit een oplossing voor de praktische problemen die vergezeld gaan met ionuitwisseling; de metalen worden geëxtraheerd als anionische chlorocomplexen en omdat een chloride-gebaseerde ionische vloeistof gebruikt wordt is er geen nettoverlies van de ionische vloeistof ionen naar de waterfase. De scheiding van kobalt en nikkel vertoont een zeer hoge selectiviteit van ongeveer $5{\cdot}10^4$. De eigenschappen van de extractiefase en de extractieparameters worden besproken en vergeleken met andere fosfonium- en ammonium ionische vloeistoffen. Dit ionische vloeistof scheidingsproces is dan verder opgeschaald tot een continu proces op laboschaal dat aantoont dat dit proces, mits optimalisaties, kan concurreren met huidige industriële processen. Dit werk is een beduidende voorwaartse stap in het ontwikkelen van een competitief industrieel proces waarbij ionische vloeistoffen als extractiefase gebruikt worden.

Door hun ionische aard zijn ionische vloeistoffen in staat om water te absorberen. Het tweede gedeelte beschrijft dat dit gedrag ten goede kan worden aangewend voor de aanmaak van een water verzadigde zure oplossing van trihexyl(tetradecyl)fosfoniumchloride waarin metaaloxiden (CaO, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO) in de ionische vloeistoffase kunnen oplossen. Dit brengt mogelijkheden met zich mee om bepaalde metalen die niet geëxtraheerd kunnen worden, toch in de ionische vloeistoffase te verkrijgen en ze dan vanuit de ionische vloeistoffase te verwerken. Verder wordt de terug-extractie (of het strippen) van deze opgeloste metalen naar de waterfase onderzocht.

In een derde gedeelte wordt er voor een andere aanpak geopteerd met betrekking tot het gebruik van ionische vloeistoffen bij de scheiding van metalen. Hierbij wordt zowel de waterfase als de organische fase vervangen door twee onderling onmengbare ionische vloeistoffen. Het scheidingsprincipe van metalen door herverdeling tussen de twee onderling onmengbare ionische vloeistoffen wordt gegeven en het process wordt toegepast voor de scheiding van kobalt en nikkel. In het proces wordt kobalt selectief geëxtraheerd van 1-ethyl-3-methylimidazolium chloride naar trihexyl(tetradecyl)fosfonium bis-[2,4,4-trimethylpentyl]fosfinaat. De processtappen zoals het wassen, het strippen en het regenereren van de ionische vloeistoffase worden verder besproken.

Het laatste gedeelte beschrijft het oplossen van metaaloxiden in imidazolium-gebaseerde ionische vloeistoffen. Alhoewel ionische vloeistoffen over het algemeen lage oplosbaarheden van metaaloxiden vertonen wordt er aangetoond dat metaaloxiden oplossen in bepaalde imidazolium-gebaseerde ionische vloeistoffen. Door de reactie tussen zilver(I)oxide met de imidazoliumringen, die een waterstof atoom in de C2-positie bezitten, worden zilver(I)carbeen complexen gevormd. De aanwezigheid van carbenen in oplossing wordt gedetecteerd door ^{13}C-NMR spectroscopie en de reacties worden opgevolgd door Ramanspectroscopie. Het oplossen van andere metaaloxiden, namelijk koper(II)oxide, zink(II)oxide en nikkel(II)oxide in imidazolium ionische vloeistoffen worden bestudeerd en stabiele zink(II)carbeen complexen in de oplossing worden gevormd.

CONTENTS

OUTLINE

This dissertation is an assembly of peer-reviewed articles, each chapter comprises one publication which contributes to the general objective of this PhD thesis. The dissertation contains four main parts preceded by an introduction (*Chapter 1*). The introduction will guide the reader through a general overview of ionic liquids and metal refining in ionic liquids. The reader will become familiar with the concepts and challenges associated with the use of ionic liquids in mineral and metal oxide processing and solvent extraction.

The first part (Chapters 2-3) demonstrates the use of the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos IL®101) as extraction phase for the extraction and separation of metal ions. *Chapter 2* illustrates the separation of cobalt from nickel from aqueous chloride solutions by selective cobalt extraction. This extraction process is proposed as a green extraction process because of the intrinsic properties related to ionic liquids. In addition, the process solves the intrinsic problem of ionic liquids in metal ion extraction, namely ion exchange. The extraction parameters and physiscal properties of trihexyl(tetradecyl)phosphonium chloride (Cyphos IL®101) are discussed in detail and compared with other ionic liquids. *Chapter 3* presents and upscaling of the process described in Chapter 2 and illustrate a lab pilot-scale continuous process which is a significant step forwards towards designing a competitive industrial process.

The second part (*Chapter 4*) describes the possibility to directly dissolve metal oxides (CaO, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO) in an acid saturated ionic liquid. In addition, the back-extraction behaviour of the different metal ions to the aqueous phase is investigated.

The third part (*Chapter 5*) presents the proof of principle for the separation of metals by solvent extraction by using two mutually immiscible ionic liquids. Cobalt was extracted from 1-ethyl-3-methylimidazolium chloride and selectively separated from nickel to trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos IL®104) and the required processing steps such as washing, stripping and regeneration of the ionic liquid phases are discussed.

In the last part (*Chapter 6*) the dissolution of metal oxides (Ag_2O, NiO, CuO, ZnO) in imidazolium ionic liquids is investigated and proof for the formation of complexes with imidazolium moieties by carbene formation is given.

The dissertation then concludes with the conclusions and future perspectives (*Chapter 7*) for the use of ionic liquids in the application field of metal processing.

NOMENCLATURE

ϵ_0	electric permittivity in vacuum
18C6	18-crown-6
[BMpyr]	1-butyl-1-methylpyridinium
[C_2mim]	1-ethyl-3-methylimidazolium
[C_4tmsim]	1-butyl-3-trimethylsilylimidazolium
[C_4mim]	1-butyl-3-methylimidazolium
[C_5mim]	1-methyl-3-pentylimidazolium
[$C_x$mim]	1-alkyl-3-methylimidazolium
[DS]	dodecylsulfate
[F-$C_x$mim]	1-fluoroalkyl-3-methylimidazolium
[Hbet]	betainium
[HSO_4]	hydrogensulfate
[$N_{221}(CH_2)_2$OMe]	*N*,*N*,-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium

$[N_{8888}]$	tetraoctylammonium
[NfO]	nonafluoro-1-butanesulfonate
$[NTf_2]$	bis(trifluoromethylsulfonyl)imide
$[PF_6]$	hexafluorophosphate
$[R_fBF_4]$	perfluoroalkyltrifluoroborate
$\%E$	extraction percentage
D_M	distribution coefficient
d	interionic distance
E	electrostatic potential
M	Madelung constant
x	mole fraction
Z^+	positively charged ion
Z^-	negatively charged ion
bif-ILs	bifunctional ionic liquids
BobCalixC6	calix[4]arene-bis-*t*-octylbenzo-crown-6
BPC6	bis(2-propyloxy)calix[4]crown-6
CDAA	*o*-carboxyphenyldiazoamino-*p*-azobenzene
CMPO	carbamoylmethylphosphine oxide
Cy272	bis-(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272)
DCH18C6	dicyclohexano-18-crown-6
DES	deep-eutectic solvents
DHS	dihexylsulfide
DtB18C6	di-*t*-butylcyclohexano)-18-crown-6
DTBSF	3,5-di-*t*-butylsalicylfluorone
EXAFS	Extended X-ray Absorption Fine Structure
H2βDA18C6	β-diketone substituted diaza 18-crown 6

Hbfa	benzoyltrifluoroacetone
HDEHP	bis-(2-diethylhexyl)phosphoric acid
HDz	dithizone
Hnta	2-naphthoyltrifluoroacetone
Hq	8-hydroxyquinoline
HRsq	8-sulfonamidoquinoline derivatives
Htaa	trifluoroacetylacetone
Htta	2-thenoyltrifluoroacetone
IL	ionic liquid
ILs	ionic liquids
IX	ion exchange mechanism
LLE	liquid-liquid extraction
LLME	liquid-liquid micro-extraction
MBASF	methybenzeneazosalicylfluorone
MBDA	N,N,N',N' -dimethyldibutyl-3-oxapentanediamide
MCILs	metal-containing ionic liquids
MeCN	acetonitrile
$NaBPh_4$	tetraphenylborate
NHCs	N-heterocyclic carbenes
PAN	1-(2-pyridylazo)-2-naphthol
PGMs	platinum group metals
PIMs	polymer inclusion membranes
RSSR	disulfide
RST	regular solution theory
SAR	structure-activity relationships
SLMs	supported liquid membranes

TAN	1-(2-thiazolyl)-2-napthol
TBDA	*N*,*N*,*N*′,*N*′ -tetrabutyl-3-oxapentanediamide
TBP	tributylphosphate
TODGA	*N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide
TOPO	trioctylphosphine oxide
TPEN	*N*,*N*,*N*′,*N*′ -tetrakis(2-pyridylmethyl)ethylenediamine
TSILs	Task-Specific Ionic Liquids

CHAPTER

1

INTRODUCTION

1.1 Ionic liquids: now there is a solution

Chemical reactions take place largely in a solution, and any liquid substance might be used as solvent.[1] Based on their degree of ionicity, solvents can be divided into three main classes (Figure 1.1). The first class, the *molecular solvents*, consists solely of neutral molecules, such as heptane, toluene or acetone. *Partially ionized solvents* form the second class. For instance, water partly dissociates to hydroxonium and hydroxide ions, in very low concentrations (10^{-7}M). Furthermore, aqueous electrolyte solutions of salts, acids or bases, in which the ions are solvated by neutral water molecules, can be considered as partially ionized solvents. Within the third class, of *completely ionized liquids*, a difference can be made between molten salts and ionic liquids; the former have a high melting point (i.e. above 100 °C), the latter a melting point below this limit. The barrier of 100 °C is arbitrarily chosen because of historical reasons and has no physical or chemical significance.[2] Some examples of molten salts are molten sodium chloride (> 801 °C), molten cryolite (>1012 °C) and molten FLiBe, which is a mixture of BeF_2 and LiF (>360°C). Ionic liquids (ILs) can be defined as liquids that consist entirely of positive and negatively charged ions and have a melting point below 100 °C. It is a relatively new class of solvents and only known since 1914.[2] Ionic liquids are formed by a suitable combination of an

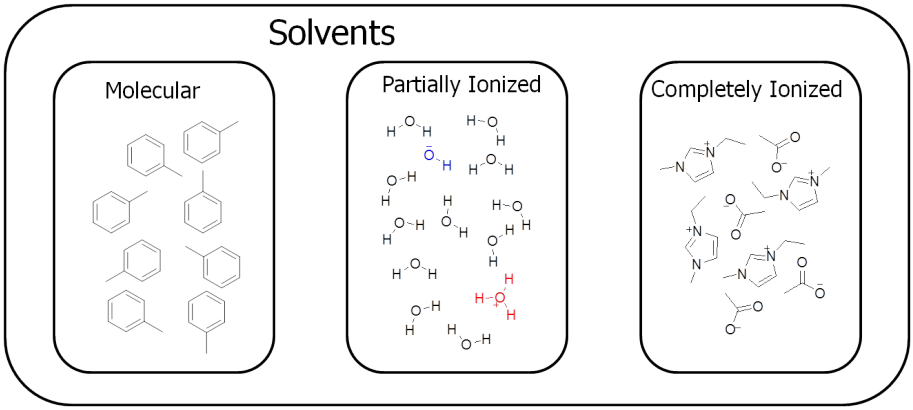

Figure 1.1: Three solvent classes

organic cation and a counter anion and some examples are given in Figure 1.2 and Figure 1.3, respectively.[1]

There are three aspects which influence the melting point in ionic compounds: the charge, size and charge distribution of the ions.[3] Hence, these aspects describe the main differences between the *high temperature molten salts* and *room temperature ionic liquids*. This can be rationalized, considering the *electrostatic potential* (E) expressed in terms of their lattice energy (equation 1.1):

$$E = \frac{M}{4\pi\epsilon_0}\frac{Z^+Z^-}{d} \tag{1.1}$$

where Z^+ and Z^- are the charges of the ions, M is the Madelung constant and d is the interionic distance between the two charges. An increased interionic distance, a lower packing efficiency (embedded in the Madelung constant) and a lower charge density, induced by delocalization of the charge over the entire ion, give rise to much lower lattice energies and thus low melting temperatures. As the ions of the molten salts can rather be described as small and having a high charge density, the ions of ionic liquids are fairly portrayed as monovalent, relatively big, asymmetrically shaped and having a diffuse charge density. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)limide can be considered as a prototype ionic liquid with a melting point of -17 °C (Figure 1.4). It seems ambiguous that only the melting point makes ionic liquids belong to a distinct solvent class, different from the molten salts. However, the practical difference, namely, that ionic liquids can be handled like ordinary solvents, is a sufficient condition to justify a separate solvent class.[4] In addition, their ion-ion interactions, which are not

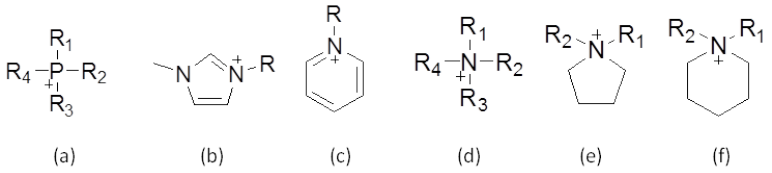

Figure 1.2: Commonly used cations in ionic liquids: (a) quaternary phosphonium; (b) 1-alkyl-3-methylimidazolium; (c) 1-alkylpyridinium; (d) quaternary ammonium; (e) 1,1'-dialkylpyrrolidinium; (f) 1,1'-dialkylpiperidinium.

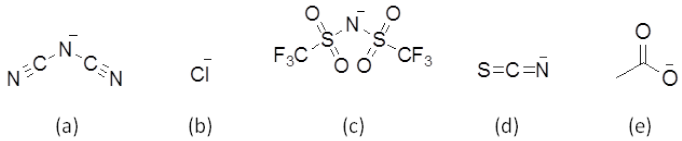

Figure 1.3: Commonly used anions in ionic liquids (a) dicyanamide; (b) chloride; (c) bis(trifluoromethylsulfonyl)imide; (d) thiocyanate; (e) acetate.

often seen in molten salts, form a more fundamental base for their subdivision. Besides the prevalent coulombic forces, other forces are involved: the Van der Waals force between the alkyl chains substituents, induced dipoles via H-bonding and π-π interactions between aromatic moieties. In general, the polarity of ionic liquids is comparable with those of short to medium chain alcohols.[3] Apart from their different features from the molten salts, the specific properties of ionic liquid further differentiate them from molecular solvents. These properties include a low vapor pressure, large electrochemical window, broad liquidus range, reasonable conductivity and a high thermal stability.[1,3] The low vapor pressure can be ascribed to the ionic character of the ionic liquid; except in plasma, ions cannot exist in gas phase and hence ion pair formation is required for them to escape to the atmosphere. Under ambient conditions these ion pairs are not formed and hence ionic liquids do not show a measurable vapor pressure. Therefore, they are considered non-flammable and non-volatile; however, under extreme conditions, a combination of low pressure and high temperature, ionic liquids are able to evaporate.[5–7]

Although each ionic liquid possesses these general properties, it has to be stated that there are huge differences in physical properties among ionic liquids such as viscosity, density, melting point and water miscibility. For instance the viscosities of ionic liquids range from 10 cP to above 1000 cP, depending on the nature of the ions. By exchanging chloride anions with hexafluorophosphate [PF_6] in [C_2mim]Cl, the water miscibility will be changed from totally water soluble to immiscible with

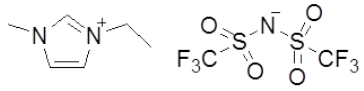

Figure 1.4: Chemical structure of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_2mim][NTf_2] (mp = -17 °C).

water; the lypophilicity of ionic liquids can be further altered by substitution of the cation. This gives the opportunity to tune and select a proper combination of ions with specific properties for a particular application. Therefore ionic liquids are considered as "designer solvents".

Ionic liquids can dissolve a wide variety of solutes both organic and inorganic compounds and uncommon combinations of compounds can be brought in the solutions.[1,3] Although coulombic forces are always prevalent, other molecular forces make ionic liquids suitable as solvents for compounds. For instance the solubility of aromatic compounds can be enhanced through $\pi - \pi$ interactions, polar or dipolar solutes can be dissolved through hydrogen-bond donor and hydrogen bond accepting abilities and metal salts through coordination of the metal ions with the IL-ions.

Ionic liquids can be designed to be immiscible with non-polar organic solvents by using hydrophilic ions, such as [C_2mim] or Cl^-, but introducing hydrophobic ions, [N_{8888}] or [NTf_2], they are immiscible with water and can thus operate in aqueous biphasic systems. The fact that ionic liquids can dissolve a variety of compounds and can be made water- immiscible makes them perfectly suitable to operate in a biphasic system for catalysis purposes.[8–14] Ionic liquids with reasonable conductivity (> 5 mS cm^{-1}) and low viscosity (< 50 cP) are suitable for a whole range of electrochemical applications. These include lithium-ion batteries, capacitors, fuel cells, electro synthesis, electrodeposition of reactive metals and nuclear waste treatment.[15–17] Other application fields in which ionic liquids have been used are membrane technology,[18–20] separation technology,[20] nanotechnology,[21–23] and analytical chemistry.[24,25]

Since impurities such as halides, water and co-solvents, possibly introduced during the synthesis of an ionic liquid, can have drastic effects on the physicochemical properties of the ionic liquid, the purity of the IL must always be reported. The corrosive nature of chloride ions in ionic liquids is of importance for process engineers.[26]

In literature the statement *ionic liquids are green solvents* is regularly seen.[27–29] The term *green* refers to green chemistry which is concerned with reducing the chemical process waste to zero and eliminating the usage and generation of hazardous

chemicals, hence contributing to a clean and safer environment.[30,31] Although the green credentials of ionic liquids are primarily attributed to their negligible vapor pressure, inhibiting their escape to the environment by air pollution, yet ionic liquids are not intrinsically green chemicals. They can be designed to be green but they can also be designed to be toxic. For instance, combinations with toxic cyanide ions can be synthesized. The communication about the hydrolysis of the hexafluorophosphate and tetrafluoroborate anions releasing hydrofluoric acid, made the ionic liquid community shudder and told us to be careful when labeling ionic liquids as green chemicals.[32] Furthermore, because most ionic liquids are soluble in aqueous solution, their loss to the environment is quite easily manageable and because of their chemical stability they will persist in the environment. Jastorff et al. presented a strategy for a sustainable evaluation of chemicals by using a combination of structure–activity relationships (SAR), toxicological and ecotoxicological tests, and modeling. This would help to avoid remediation measures of undesirable effects in advance of upscaling the production volume of new technologies afterwards.[33] Other techniques aimed at avoiding the release of ionic liquids into the aquatic environment include nanofiltration[34,35] and salting-out processes using electrolytes,[36–38] carbon dioxide,[39] or carbohydrates.[40]

Ionic liquids can be subdivided based on their chemical composition, and several concepts often occurring in the ionic liquid research field are shortly described below. **Functionalized ionic liquids**, or *Task-Specific Ionic Liquids* (TSILs) as described by Davis, possess functional groups covalently bonded to the IL ions.[41] Several reasons for the incorporation of functional groups can be rationalized, for instance binding or catalytic activation of a certain dissolved substrate. The first example was derived from a bioactive species, namely the antifungal drug miconazole (Figure 1.5).[42] Other objectives which can be obtained by functionalization of ionic liquids are the modification of the solvent parameters,[43] or improvement of the biodegradability.[44]

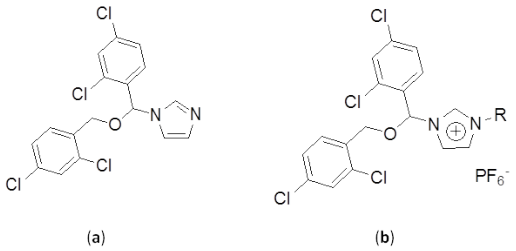

Figure 1.5: Chemical structure of (a) miconazole; (b) ionic liquid derived from miconazole with R= CH_3, Et, n-Bu, $(CH_2)_2(CF_2)_5CF_3$.

Closely related to ionic liquids are **deep-eutectic solvents** (DES).[45,46] DES are mixtures of two components mainly a quaternary ammonium halide salt and a hydrogen bond donor such as amines, alcohols or acids which form a low eutectic melt. On the foundation of this behavior lays the charge delocalization via hydrogen bonding between the hydrogen bond donor and the halide. A well known example is the mixture of choline chloride and urea. In pure state, these compounds have a melting point of 302 °C and 133 °C respectively; when they are mixed in a 1:2-ratio, an eutectic melt at 12 °C is obtained thus it is liquid at room temperature. DES have certain advantages over ionic liquids: they are easy to prepare, biodegradable, cheap and they do not react with water.

Another class of ionic liquids are the **metal-containing ionic liquids** (MCILs), these are ionic liquids for which a metal ion or metal complex is part of either the cation or the anion.[47] In MCILs the properties of ionic liquids are combined with magnetic, spectroscopic and catalytic properties depending on the incorporated metal (Figure1.6).[48–54] The first metal-containing ionic liquid was used for the electroplating of aluminum by Hurley and Wier in 1951 and was made of a binary mixture of *N*-ethylpyridinium bromide and aluminium chloride.[55] Mixtures of aluminium chloride and organic cationic halide salts form so-called chloroaluminate ionic liquids. Room temperature chloroaluminates were obtained by using $[C_2mim]$ as organic cation.[56] However, these compounds resemble a solution of aluminium chloride dissolved in an organic halide salt mixture rather than a metal-containing ionic liquid. In the region of $0.33 < x < 0.67$ (with x the mole fraction of $AlCl_3$), aluminium is fully incorporated in the anionic tetrachloroaluminate complex $[AlCl_4]^-$ (Figure 1.7). Furthermore, at mol fractions of $0.5 < x < 0.67$ there are no free chlorides left and the mixture consists of a mixture of tetrachloroaluminate $[AlCl_4]^-$ and heptachlorodialuminate $[Al_2Cl_7]^-$ anions. The interesting feature of chloroaluminate ionic liquids is that depending on the molar composition of alumina chloride, they react Lewis basic ($0.33 < x < 0.5$), neutral ($x = 0.5$) or Lewis

Figure 1.6: Response of the orange-colored $[C_6mim]_3[Dy(SCN)_6(H_2O)_2]$ ionic liquid to a neodymium magnet.
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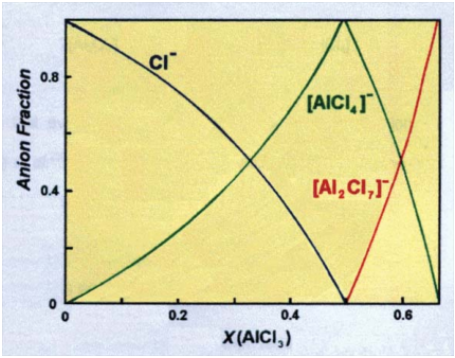

Figure 1.7: The concentration of anions in 1-ethyl-3-methylimidazolium chloride-$AlCl_3$ system as a function of composition, $X(AlCl_3)$.
(Reproduced with permission from ref. 58 ©2008 Royal Society of Chemistry)

acidic ($0.5 < x < 0.67$).[57,58] Chloroaluminates have been applied for spectroscopy, electrochemistry and synthesis. A major drawback of these compounds is their moisture sensitivity in which hydrochloric acid is generated and hence exclusion from air is absolutely necessary. This drawback drastically reduces the application field of the chloroaluminate ionic liquids.

Metal-containing ionic liquids comprising other metals than aluminium have been synthesized. These include halides of the metals Co, Ni, Mn, Cu, Zn, Sn, In, Pt, Ir, Pd, Au; carbonyls of Co and Rh and *N*-heterocyclic carbene (NHCs) complexes of silver.[47,59] Most of these MCILs are moisture and water stable and show tunable Lewis acidity. They are therefore able to mediate a wide range of chemical reactions in organometallic synthesis. As the MCIL acts both as solvent and catalyst, the catalyst leaching is negligible. In addition, other MCILs composed of thiocyanato and isothiocyanato complexes of lanthanides, cobalt and uranyl,[54,60–62] as well as oxoanion ionic liquids base of the tungstate ion have been reported.[63] The direct electrowinning of metals from ionic liquids with a metal-containing anion is not favorable. This because their concentration is potentially driven and at the required negative potential, the concentration at the cathode will be to low to initiate nucleation.[64] In contrast, ionic liquids with a metal-containing cation are much better candidates as electrolytes for electrodeposition. More recently metal-containing ionic liquids in which the metals have been incorporated in the cation are synthesized. Abood et al. showed that the addition of a simple amide, such as acetamide or urea to $AlCl_3$ causes the formation of a liquid in the form of $[AlCl_2 \cdot n\ \text{Amide}]^+[AlCl_4]^-$. From this ionic liquid alumina was electrochemically deposited on an electrode.[65]

The cyclic voltammograms of an ionic liquid which was prepared from iron(III)triflate and diethanolamine indicate that the compound displayed quasi-reversible Fe^{3+}/Fe^{2+} reduction and oxidation behaviour.[66] Furthermore, similar metal-containing ionic liquids of copper, zinc and manganese have been prepared.[67,68] Brooks et al. synthesized cationic cuprous organic complexes of the type $[Cu(MeCN)_x][NTf_2]$ (with $x = 2-4$ and MeCN = acetonitrile), which could be used for high current density electrodeposition.[69] Similarly, other elements and ligands were tried to be incorporated in the metal-containing cations.[64,70–73] Examples of ionic liquids with organometal-containing cations was reported by Gao et al. who synthesized (ferrocenylmethyl)imidazolium and (ferrocenylmethyl)triazolium room temperature ionic liquids which may be useful in applications for inhomogeneous catalysis as well as in biological systems.[74]

A whole range of industrial applications of ionic liquids already applied in the chemical industry are discussed by Plechkova and Seddon.[58] In all the given examples the particular ionic liquids show specific advantages over the current state which allow them to be applied in industry. Some examples are the use of ionic liquids as: an acid scavenger in the BASIL process (*Biphasic Acid Scavenging utilizing Ionic Liquids*), azeotrope breakers, a phosgene substitute, cellulose dissolution medium, Lewis basic catalyst in the isomerisation process of 3,4-epoxybut-1-ene to 2,5-dihydrofuran, paint additives, electrolyte in lithium-ion batteries and the ionic compressor.

The ionic liquid research field is popular and the number of scientific publications containing the concept ionic liquid is still increasing each year (up to 6300 in 2013 in Web of Science). The fact that ionic liquids are voted as the most important British innovation of the 21^{st} century confirms its popularity.[75] The broad range of industrial application fields are conclusive that ionic liquids are ready for a breakthrough. In the 1990's the suppliers of ionic liquids were scarce; nowadays many ionic liquid suppliers are known which provide ionic liquids from gram to the multi-ton scale. Some example of suppliers are Merck, Iolitec, Cytec, BASF. However, there are other challenges which need to be mastered before ionic liquids could be applied in industry. For instance the price of ionic liquids, which is high compared to the price of organic solvents. In general, the price of ionic liquids will be 5 to 20 times higher than molecular solvents.[58] Recycling 10 to 20 times will be necessary to reach the same cost as molecular solvents. Production on ton scale will further lower the price. Furthermore, the toxicity and environmental impact of ionic liquids and the products of their breakdown must be fully understood before ionic liquids can be industrially implemented.[76,77] In addition, the long term stability and recyclability under process relevant conditions together with a model to predict physicochemical data relevant for its applications will be necessary.

1.2 Metal processing in ionic liquids

Hydrometallurgical processes are used for the processing and reprocessing of metal ores. Since the last decades environmental regulations are bringing up new challenges for waste water treatment. For instance, the neutralization of acidic and alkaline conditions bringing up salt discharge concerns, furthermore the need to dilute heavy metals to extremely low metal concentrations demands large amounts of water being both energy and labor intensive.[78] Therefore, water as a green solvent can be argued in hydrometallurgical processes. From hydrometallurgical point of view, ionic liquids can have some benefits over the use of water as media for metal processing. The volume of low level aqueous streams that needs to be processed will significantly be reduced and the process can be intensified by improved extraction efficiency in a biphasic process. In addition, the non-volatility of ionic liquids can allow leaching of metal ores at elevated temperatures without the need for an autoclave. This section will review the literature about the processing of metals in ionic liquids and related solvents.

1.2.1 Mineral and metal oxide processing in ionic liquids

In spite of the opportunities mentioned previously, only a few studies of metal oxide dissolution in ionic liquids are done.[78,79] The specific problem associated with the dissolution of metal oxides is the need for an oxide-binding agent, by which the oxide reacts and can be replaced with other ligands. In commonly used ionic liquids, these oxide-binding species are not present. Therefore, low solubilities for metal oxides are generally found. However, an ionic liquid containing coordinating ions and oxide-binding species such as acidic protons can react with the metal oxide and the metal ion will then be solvated by the coordinating ions of the ionic liquid. The first publication on the dissolution of a metal oxide in ionic liquids was reported by Dai et al. in 1997.[80] They investigated the solubility of uranium(VI) oxide in imidazolium chlororoaluminate ionic liquids. Bell et al. reported on the dissolution of vanadium(V)oxide (V_2O_5) in imidazolium chlororoaluminates and found different species as function of the melt acidity.[81] However, chloroaluminate ionic liquids are water sensitive and cannot be used for metal process purposes.

Abbott and coworkers were able to dissolve a wide variety of metal oxides in deep-eutectic solvents (DES). They reported the solubility of copper(II) oxide, zinc(II) oxide and iron(II,III) oxide in three different deep eutectic solvents formed by a mixture of choline chloride and a carboxilic acid, namely, malonic acid, oxalic acid and phenylpropionic acid.[46] High solubilities were achieved for all three oxides, but the most important observation was that the solubility of each oxide is markedly different in each DES even to the extent that the order of solubility

changes. They found that the more ionic transition metal oxides were soluble whereas more covalent metal oxides such as alumina and silicate were not. Therefore, they suggested that metal ions could be extracted from aluminosilicates without dissolving the matrix. Furthermore, seventeen metal oxides in the elemental mass series titanium through zinc were determined in three DES, namely, mixtures of choline chloride with malonic acid (1:1), urea (1:2) and ethylene glycol (1:1).[82] They found that malonic-acid-based DES exhibited higher solubility for the metal oxides than the liquids based on urea and ethylene glycol. The more ionic oxides such as zinc(II) oxide were found to have a high solubility whereas more covalent oxides such as titanium(IV) oxide exhibit negligible solubility. They also showed the application of recovering zinc and lead from a waste material produced by the electric arc furnace (EAF) using mixtures of choline chloride and urea.[83] Zinc and lead were selectively removed and subsequently electrowon from the liquid and this allows the insoluble alumino silicates and iron oxides to be recycled. Furthermore, the design and operation of the first large scale digestion and metal recovery using a deep eutectic solvent was demonstrated.[84]

Nockemann et al. used betainium bis(trifluoromethylsulfonyl)imide ([Hbet][Tf_2N]) for the dissolution of several metal oxides including the rare-earth oxides, uranium(VI) oxide, zinc(II) oxide (ZnO), copper(II) oxide (CuO) and nickel(II) oxide (NiO).[60,85]

In the field of mineral processing, ionic liquids were applied as leach solution, Whitehead et al. used 1-butyl-3-methylimidazolium hydrogensulfate ([C_4mim][HSO_4]) as leaching media for minerals such as pyrite and chalcopyrite, in which an oxidative leach was applied to selectively extract gold and silver with iron(III)sulfate as oxidant and thiourea as complexing agent.[86,87] Furthermore, Dong et al. used [C_4mim][HSO_4] and its aqueous solutions containing oxygen as oxidant for the leaching of chalcopyrite.[88]

1.2.2 Ionic liquids in metal ion extraction

Substituting the volatile hydrocarbons, currently used as organic phase in *liquid-liquid extraction* (LLE), by ionic liquids will lead to inherently safer and environmentally friendlier extraction processes.[89] Rogers and coworkers were the first to suggest the use of ionic liquids as extraction phase for liquid-liquid extraction in 1998. They demonstrated the extraction of a variety of ionizable and non-ionizable aryl compounds to 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]).[90] An essential requirement for ionic liquids to operate in liquid-liquid extraction applications is water-immiscibility, which can be achieved by substitution with long alkyl chains or using fluorinated ions. The extraction of metal ions from an aqueous phase to hydrophobic ionic liquids will only take place if the

direct environment of the metal ion is made hydrophobic, which can be achieved by using extractants sparingly soluble in the aqueous phase. In this section the use of ionic liquids in liquid-liquid extraction of metal ions will be reviewed and the focus is on the extraction mechanism and nature of the metal ion species. This subject has also been reviewed by other authors.[77–79,91–97] Metal ion extraction to ionic liquids can be divided into groups based on the extractant, namely neutral extractants, acidic extractants, *extractant functionalized*-ionic liquids and extraction without added extractants.

Neutral extractants

The application of ILs as diluent for the extraction of metal ions was for the first time reported by Dai et al. in 1999.[98] They reported the extraction of strontium from an aqueous phase by the crown ether dicyclohexano-18-crown-6 (DCH18C6) to hexafluorophosphate and bis(trifluoromethylsulfonyl)imide alkylimidazolium ionic liquids ([$C_x$mim][[PF_6] and [$C_x$mim][NTf_2]). A remarkably high distribution coefficient for the metal ion (D_M) was found compared to similar extraction systems in molecular solvents. These findings opened perspectives for the use of ionic liquids in liquid-liquid extraction applications. Further research showed both similarities and differences in metal ion extraction between ionic liquids and molecular solvents.[99,100] These findings required a fundamental chemical understanding. Dietz and coworkers investigated the extraction process by systematically comparing the extraction of strontium with DCH18C6 in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides ([$C_x$mim][NTf_2]) with extraction in 1-octanol and they found differences between the two solvents in nearly every aspects:[101]

- Increased water content in the ionic liquid phase led to lower D_M values, whereas in 1-octanol a higher D_M values were found by increasing the water content.
- D_M increases with HNO_3 concentrations in 1-octanol, but decreases in ionic liquids.
- The differences in extraction of strontium in 1-octanol from HNO_3 and HCl were about two orders of magnitude, whereas for ionic liquids the acid dependencies differed little.
- An increase in strontium concentration was accompanied by an increased aqueous solubility of the ionic liquid cation, in contrast to 1-octanol.

All these differences made it obvious that the extraction mechanism in ionic liquids is clearly distinct from that in molecular solvents. EXAFS investigations revealed

that differences in extraction mechanism can be attributed to the nature of the extracted species.[102] For the extraction in molecular solvents the extracted species is a neutral strontium crown ether nitrato complex (Figure 1.8, a), whereas in ionic liquids the Sr–DCH18C6 complex is accompanied by two water molecules, forming a charged species (Figure 1.8, b). However, charge neutrality implies the compensation of the charged extracted species by **cation exchange**, by which a strontium crown ether complex is exchanged with the IL-cation constituent (Figure 1.9, a). This fundamental investigation about the extraction species and extraction mechanism was very important because its practical implications are enormous, as it is that the **ion exchange mechanism (IX)** forms a serious problem for possible applications of ionic liquids in liquid-liquid extraction. Because the IL cation will be lost to the aqueous phase upon metal ion extraction, this will both have a cost and environmental impact and therefore the suppression of the ion exchange mechanism is required. In literature two approaches were taken into account in order to suppress ion exchange: firstly by increasing the hydrophobicity of the ionic liquid cations through increasing alkyl chainlength,[103] and by using fluorinated alkyl chains;[104] whereas the second approach was using a sacrificial cation exchanger.[105] By altering the alkyl chain substituted on the imidazolium from C_5 to C_{10}, the aqueous solubility of the cation will be lowered, which makes ion exchange more difficult and forcing the extraction mechanism towards the extraction of the neutral complex (i.e. strontium crown ether nitrato complex). If an equal extraction percentage is observed both for strontium ($\%E_{Sr}$) and nitrate ($\%E_{NO_3}$), the neutral nitrato complex will be extracted; whereas if $\%E_{Sr}$ will be much higher than $\%E_{NO_3}$, ion exchange will occur. By increasing the alkyl chain length from C_5

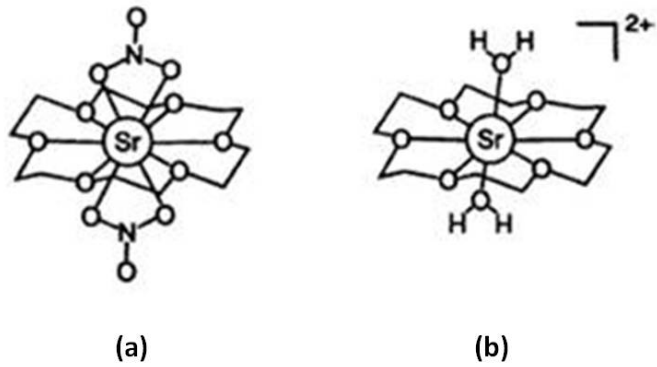

Figure 1.8: Coordination environments of $Sr(NO_3)_2$(DCH18C6) in 1-octanol (a) and the Sr(DCH18C6)$(H_2O)_2^{2+}$ cation present in $[C_5mim][NTf_2]$ (b).
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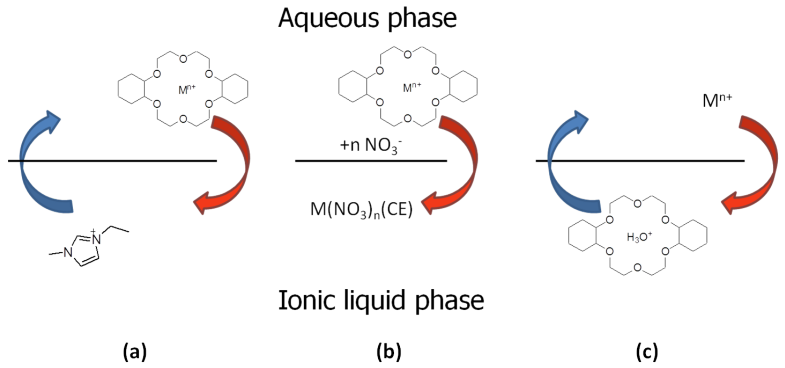

Figure 1.9: Three-path model for metal ion partitioning between nitric acid solution and $[C_2mim][NTf_2]$ ionic liquid in the presence of DCH18C6. Ion exchange (a); extraction via neutral complex (b); ion exchange via DCH18C6 : hydroxonium adduct (c).[107,108]

to C_{10}, one observed a gradual increase of $\%E_{NO_3}$ and even for C_{10} equal extraction percentage for strontium and nitrate were found which means that a neutral complex was extracted. The cost one had to pay was a decrease in $\%E_{Sr}$ from 96 to 20 by increasing chain length from C_5 to C_{10} respectively. However, increasing the alkyl chain length was not sufficient to eliminate ion exchange since a ternary extraction mechanism was found by which a DCH18C6 : hydroxonium adduct is exchanged by the metal ion.[106] Although no IL cation was directly exchanged, in advance of this exchange, the DCH18C6 : hydroxonium adduct has been exchanged for the IL cation. Therefore, the overall extraction process can best be described by three processes (Figure 1.9), namely the exchange of metal–crown ether complex for the IL cation (equation 1.2), the neutral metal nitrato–crown ether complex partitioning (equation 1.3) and the crown ether-mediated M^+/H_3O^+ exchange (equation 1.4). The weight for each mechanism is determined by the hydrophobicity of the IL cation and the aqueous acidity.[107,108]

$$M \cdot DCH18C6^{n+} + C_x mim^+_{IL} \rightarrow M \cdot DCH18C6^{n+}_{IL} + C_x mim^+ \tag{1.2}$$

$$M^{n+} + n\mathrm{NO_3} + DCH18C6_{IL} \rightarrow M \cdot DCH18C6^{n+}_{IL} \tag{1.3}$$

$$M^{n+} + \mathrm{H_3O} \cdot DCH18C6^{+}_{IL} \rightarrow \mathrm{H_3O^+} + M \cdot DCH18C6^{n+}_{IL} \tag{1.4}$$

Fluorination of alkyl chains substituted on the imidazolium cation was not significantly more effective at surpressing IX than increasing the alkyl chainlength

and even lower extraction efficiencies than for 1-octanol were obtained.[104] The second approach to overcome ion exchange was by making use of a sacrificial cationic species.[105] These sacrificial cations, dissolved in the ionic liquid phase, will be transferred to the aqueous phase upon metal ion extraction in preference of the IL cation. Extraction of cesium to $[C_4mim][NTf_2]$ by the extractant bob-CalixC6 using sodium tetraphenylborate ($NaBPh_4$), for which sodium acts as the sacrificial cation, a reduction in the loss of IL cation was observed but the exchange with the IL cation could not be fully eliminated and thus reduced rather than eliminated the IL cation exchange. Besides the extensively discussed ion exchange, the use of extraction systems with neutral extractants has another disadvantage, namely that the back extraction or stripping of the metal ions is difficult;[91] only a few reports showed the back-extraction with aqueous acid solutions.[109–112] In Table 1.1 most of the work on extraction system with neutral extractants in ionic liquids is reported.

Table 1.1: Metal ion extraction with neutral extractants and ionic liquids.

Metal ion	**Extractant**	**Ionic Liquid**	**Year of publication**	**Ref.**
Sr^2+	DCH18C6	[C$_x$mim][PF$_6$], [C$_x$mim][NTf$_2$]	1999	98
Sr^{2+}, Cs^+, Na^+	18C6, DtB18C6, DCH18C6	[C$_x$mim][PF$_6$]	2000	99
Li^+, Na^+, K^+, Rb^+, Cs^+	DCH18C6	[C$_x$mim][PF$_6$]	2001	100
Sr^{2+}	DCH18C6	[C$_x$mim][NTf$_2$]	2001, 2003	101,103
Ln^{3+}	CMPO	[C$_x$mim][PF$_6$]	2003	113
UO_2^2+	CMPO-TBP	[C$_x$mim][PF$_6$], [C$_x$mim][NTf$_2$]	2003	114
UO_2^2+, Pt^{4+}, Am^{3+}, Th^{4+}	CMPO-TBP	[C$_x$mim][PF$_6$]	2003	115
Ag^+	calixarenes	[C$_x$mim][PF$_6$]	2004	110,111
Cs^+, Sr^{2+}, K^+	*N*-alkyl aza-18-crown-6	[C$_x$mim][NTf$_2$]	2004	109
Cs^+	BobCalixC6	[C$_x$mim][NTf$_2$]	2004	105
UO_2^{2+}	TBP	[C$_x$mim][PF$_6$]	2004	116
Ln^{3+}	CMPO	[C$_x$mim][PF$_6$], [C$_x$mim][NTf$_2$]	2005	117
Na^+, Ca^{2+}, Sr^{2+}	DCH18C6-TBP	[C$_x$mim][NTf$_2$]	2005	118
UO_2^{2+}	TBP	[C$_x$mim][PF$_6$]	2005	119
Sr^{2+}	DCH18C6	[F-C$_x$mim][NTf$_2$]	2006	104
Ln^{3+}	TPEN	[C$_x$mim][PF$_6$]	2006	112
UO_2^{2+}	TBP	[C$_x$mim][NTf$_2$]	2008	120
Am^{3+}	CMPO-TBP	[C$_x$mim][NTf$_2$]	2009	121
In^{3+}	TOPO	[C$_x$mim][NTf$_2$]	2009	122
Cs^+	BPC6	[C$_x$mim][NTf$_2$]	2010	123
Eu^{3+}	CMPO-TBP	[C$_x$mim][NTf$_2$]	2011	124
UO_2^{2+}	TBDA, MBDA	[C$_x$mim][PF$_6$]	2011	125
UO_2^{2+}	TBP	[C$_x$mim][NTf$_2$]	2011	93
Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}	DCH18C6	[C$_x$mim][NTf$_2$]	2012	107,108
Rh^{3+}	CMPO, TODGA, TBP, DHS	[(CH$_3$)$_3$NCH$_2$CH$_2$OMe][NTf$_2$]	2012	126

Acidic extractants

Using acidic extractants can be advantageous over using neutral extractants because of the tunable pH of the aqueous phase by which the selectivity of the metal ion extraction can be controlled and also because of the ease of back-extraction.[91] Visser et al. were the first to use acidic extractants in ionic liquids.[89,127] They used 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-thiazolyl)-2-napthol (TAN) to extract a variety of metal ions from aqueous to ionic liquid solution ($[C_4mim][PF_6]$). Jensen et al. elucidate the extraction mechanism for lanthanides (Eu^{3+}, Nd^{3+}) with 2-thenoyltrifluoroacetone (Htta) in $[C_4mim][NTf_2]$ by using complementary physicochemical methods: optical absorption and luminescence spectroscopies, molecular dynamics simulations, equilibrium thermodynamics, high-energy X-ray scattering, and EXAFS.[128] They found the formation of anionic complexes $[Nd(tta)]_4^-$ or $[Eu(tta)]_4^-$. Since no Na^+ or H^+ was extracted to the ionic liquid phase, the anionic constituent $[NTf_2]$ has to be exchanged with $[Ln(tta)]_4^-$ upon extraction (Figure 1.10, b). Whereas in molecular solvents rather neutral $M(tta)_3(H_2O)_n$ (with n = 2 or 3) complexes were formed; extraction of anionic complexes in molecular solvents have only been observed when hydrophobic counter ions were used such as tetraalkylammonium salts.[129] This **anion exchange** has implications for the greenness and long term practicability of the extraction process because the fluorinated anions will be lost to the aqueous phase.

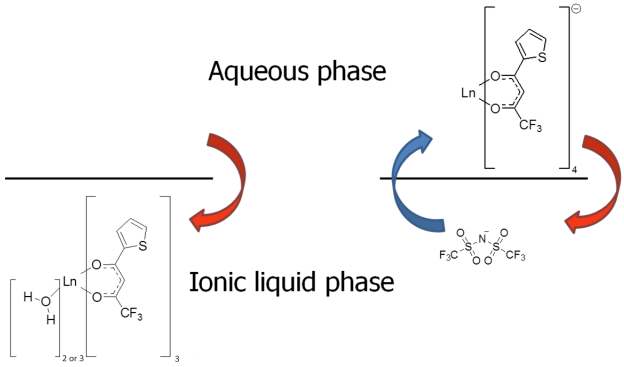

Figure 1.10: Extraction mechanisms for Ln^{3+} with Htta in $[C_4mim][NTf_2]$: via neutral complex extraction (a); via anion exchange (b).[127,130]

However, other publications show that the extraction mechanism is not necessarily forced to undergo anion exchange and the extraction of neutral complexes or mixed complexes have been reported. Jensen et al. found by using low Htta concentrations ($< 10^{-6}$ M) that Nd^{3+} and Eu^{3+} were extracted as neutral $M(tta)_3(H_2O)_x$ complexes, where x = 2 or 3 (Figure 1.10, a).[130] The affinity of the neutral complex for the ionic liquid was comparable with alcohols and ketones and was two orders of magnitude larger than aliphatic, aromatic or halogenated solvents. Also, by changing the IL anion $[NTf_2]$ to nonafluoro-1-butanesulfonate ([NfO]) the anionic complex $[Ln(tta)_4]^-$ was not found for Eu^{3+} and Nd^{3+}, but they were extracted as other metallic species.[131] Namely, at low pH or low extractant concentrations, the lanthanides were extracted from 1M $NaClO_4$ solutions into $[C_4mim][NfO]$ as the fully hydrated aqua cations ($Ln(H_2O)_9^{3+}$). By increasing the extractant concentration and pH, other complexes with a different number of coordinated tta-anions (2 or 3) and different number of water molecules (0 or 2) were extracted and in order to complete the coordination sphere additional complexation by either [NfO] or $[ClO_4]$ was required. The change in extraction mechanism by changing the IL-anion from $[NTf_2]$ to[NfO] was ascribed to the enhanced water solubilities in $[C_4mim][NfO]$ compared to $[C_4mim][NTf_2]$. Hirayama et al. observed that neutral hydrated complexes $M(tta)_2(H_2O)_n$ (with M = Ni, Cu, Pb) were extracted to $[C_4mim][PF_6]$ as this is the case for molecular solvents, whereas for other metals, anionic species $[M(tta)_3]^-$ (with M = Co, Zn and Cd) were observed.[132] Changing the IL anion to $[NTf_2]^-$ for Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} and Cd^{2+}, anionic complexes were extracted; whereas Cu^{2+} was still extracted as a neutral complex.[133] The regular solution theory (RST) was applied for numerical calculation for the evaluation of the distribution coefficients of Htta, $Cu(tta)_2$ and $Ni(tta)_2$ and compared with various molecular solvents. The ionic liquid solution containing Htta can be seen as a regular solution similar to organic solvents, whereas the effect of ionic liquids on the D_M of the metal complexes is rather complex. It was found that the neutral complex $Cu(tta)_2$ in $[C_4mim][NTf_2]$ was rather similar to that of non-polar organic solutions, whereas $Ni(tta)_2$-IL solution showed large deviation from the regular solutions and was rather similar to ether and ketone solutions.[134] Lertlapwasin et al. report the extraction of Ni^{2+}, Cu^{2+} and Pb^{2+} with $[C_4mim][PF_6]$ containing 2-aminothiophenol.[135] For Ni^{2+} and Pb^{2+} they reported a proton transfer mechanism and Ni^{2+} and Pb^{2+} were respectively extracted as ML_3^- and ML_2; whereas copper was extracted, via a redox mechanism, as a monovalent copper complex ML_2^- for which the oxidation of two 2-aminothiophenol to a disulfide (RSSR) by Cu^{2+} was proposed. Other research confirmed similarities between the extraction behavior of metal ions to ionic liquids and to molecular solvents.[136–138] In contrast to metal extraction in ionic liquids using neutral extractants, which is different to the extraction in molecular solvents; acidic extractants are directly comparable with the extraction in molecular solvents. On the other hand the extraction of a neutral species is disadvantageous because not the full advantage has been taken about the unique ionic liquid environment.

A combination of an acidic extractant and a neutral extractant were used for the extraction of lanthanides by Hirayama and coworkers.[139,140] In particular, lanthanides were extracted with Htta in combination with crown ethers to $[C_4mim][NTf_2]$ as cationic ternary complexes $(Ln(tta)_2(CE)^+$ and $Ln(tta)_2(CE)^{2+})$. The extraction process was named an *ionic liquid synergistic cation-exchange system* for which the synergistic effect was thought to be due to the size fitting of CE on complexation to Ln^{3+} and neutral or anionic extracted species were converted to cationic ternary complexes for which extraction enhancement was reported. Intramolecular synergistic extraction for which an intramolecular β-diketone substituted diaza 18-crown-6 (H2βDA18C6) in $[C_2mim][NTf_2]$ was used for the extraction of strontium has been reported by Shimojo et al. and Sr^{2+} could be recovered from the ionic liquid under acidic conditions.[141] Table 1.2 summarizes most of the work on extraction system with acidic extractants in ionic liquids.

Table 1.2: Metal ion extraction combining acidic extractants and ionic liquids.

Metal ion	**Extractant**	**Ionic Liquid**	**Year of pub.**	**Ref.**
Co^{2+}, Ni^{2+}, Fe^{3+}, Cd^{2+}, Hg^{2+}, Na^{+}	PAN, TAN	$[C_x\text{mim}][PF_6]$	2001	127
Cu^{2+}	HDz, Hq, PAN	$[C_x\text{mim}][PF_6]$	2003	138
Cd^{2+}, Hg^{2+}, Ag^{+}, Pb^{2+}, Ln^{3+}	HDz	$[C_x\text{mim}][PF_6]$	2003	137
Ln^{3+}	Htta	$[C_x\text{mim}][NTf_2]$	2003	128
UO_2^{2+}, Ln^{3+}, Am^{3+}	Cy272, HDEHP	$[C_x\text{mim}][NTf_2]$	2005	130,136
Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}	Htta	$[C_x\text{mim}][PF_6]$	2005	132
Ge^{4+}	MBASF	$[C_x\text{mim}][PF_6]$	2006	142
Mn^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}	Hq	$[N_{221}(CH_2)_2\text{OMe}][NTf_2]$	2006	143
Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}	Hnta, Hbfa, Htta, Htaa	$[C_x\text{mim}][PF_6]$	2006	144
Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}	Htta	$[N_{8888}][DS]$	2006	145
Pb^{2+}	HDz	$[C_4\text{tmsim}][PF_6]$	2007	146
Hg^{2+}	CDAA	$[C_4\text{tmsim}][PF_6]$	2007	147
Al^{3+}	DTBSF	$[C_x\text{tmsim}][PF_6]$	2007	148
Pb^{2+}	HDz	$[C_x\text{mim}][PF_6]$	2007	149
Zn^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cu^{2+}	Htta	$[C_x\text{mim}][NTf_2]$	2008	133
Co^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}	HRsq	$[C_x\text{mim}][PF_6]$	2008	150
Ag^{+}, Pb^{2+}	HDz	$[C_x\text{mim}][PF_6]$, $[C_x\text{mim}][NTf_2]$	2009	151
Ni^{2+}, Cu^{2+}, Pb^{2+}	2-aminothiophenol	$[C_x\text{mim}][PF_6]$	2010	135
Ln^{3+}	HDEHP	$[C_x\text{mim}][PF_6]$, $[\text{BMpyr}][PF_6]$	2010	152
Ln^{3+}	Htta	$[C_x\text{mim}][\text{NfO}]$	2012	131

Extractant functionalized ionic liquids

Extractant functionalized ionic liquids have functional groups tethered on their cationic or anionic moiety for which the functional group acts as a complexation site able to bind metal ions. *Extractant functionalized* ionic liquids both act as solvent and as extractant and they restrain the extractant/solvent miscibility problem, the loss of chelating agent to aqueous phase, avoiding ion-exchange as extraction mechanism and pH dependent stability and pH controlled selectivity.[92,153] Disadvantages of functionalized ionic liquids are the multi-step synthesis which makes their production expensive, in addition functionalized ionic liquids usually have a high viscosity and therefore dilution into a common ionic liquid or solvent is necessary. Furthermore the influence of functional groups on the biodegradability and aquatic toxicity of functionalized ionic liquids is unknown and needs further investigation.[92,154]

The first report of functionalized ionic liquids **with a neutral complexation site** is reported by Visser et al. in 2001. They used ionic liquids for which thioether **(1)**, thiourea **(2)** and urea groups **(3)** were substituted on the alkylimidazolium cation combined with a hexafluorophosphate anion and were able to extract the heavy metals Hg^{2+} and Cd^{2+}.[153,154] Papaiconomou et al. compared the extraction of certain metal ions of a pyridinium, piperidinium and pyrrolidinium cationic core functionalized with disulfide **(4)** and nitrile **(5)** groups with unfunctionalized analogs and found an improved extraction performance for the functionalized cations.[155] Selectivity was found for extraction of Cu^{2+} and Hg^{2+} when disulfide functional groups were used; nitrile functionalized ionic liquids showed selectivity for Ag^{+} and Pd^{2+}. Besides the presence of functional groups, the physicochemical properties of the ionic liquid influenced the extraction efficiencies, depending on which cationic core was used. Lee used analogue ionic liquids for the extraction of gold, silver and palladium and he found efficient and selective gold extraction.[156] Recently a CMPO-based functionalized cation **(6)** was used for the extraction of actinides and lanthanides.[157] Luo et al. applied monoaza-crown ether substituted imidazolium **(7)** diluted in $[C_4mim][NTf_2]$ for the extraction of Cs^{+} and Sr^{2+} and a lower D_M was reported compared to the extraction of using unbonded aza-crown ether in the same ionic liquid. They addressed lower D_M values to lower complexation stability with metal cations due to coulombic repulsion, therefore other approaches come within reach.[158]

Ionic liquids functionalized **with a chelating extractant** incorporated on the cation were first reported by Ouadi et al., they used ionic liquids bearing 2-hydroxybenzylamine entities **(8)** and studied the extraction of Am^{3+}.[159] They found that the extraction system was driven by anion exchange. Furthermore, they studied the extraction of uranyl by quaternary ammonium bearing phosphoryl groups **(9)** in combination with a bis(trifluoromethylsulfonyl)imide anion.[160] Morita et

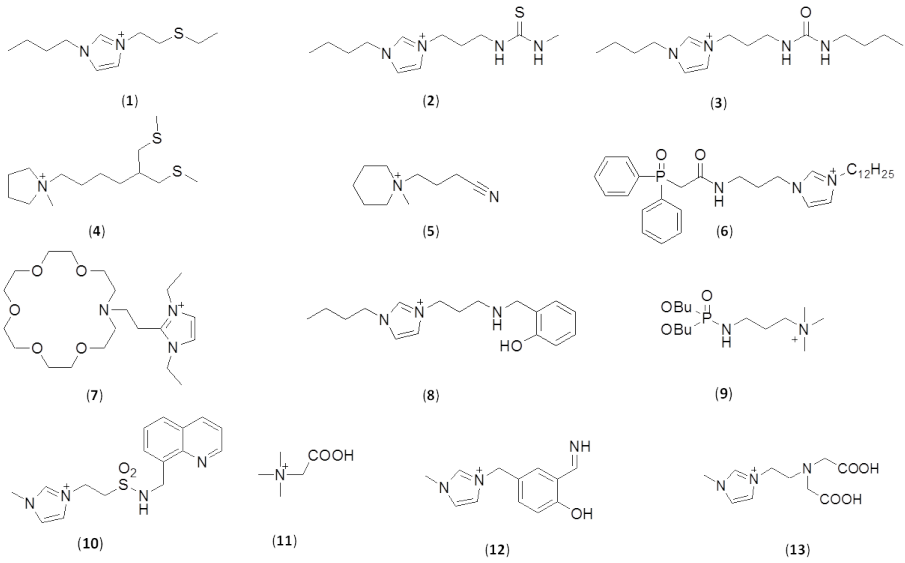

Figure 1.11: Selected *extractant functionalized* cations used for metal ion extraction to ionic liquids.

al. synthesized 1-methyl-3-[2-(8-quinolinylaminosulfonyl)ethyl]-imidazolium **(10)** chloride and evaluated the extraction of divalent metal ions (Co^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}) and relatively high extractions in comparison with non-imidazolium analogs were reported.[161] Nockemann et al. were able to dissolve various metal oxides in betainic **(11)** bis(trifluoromethylsulfonyl)imide as earlier described (section 1.2.1) and they were able to back-extract the metal ions to acidic aqueous phase.[60,85] Singer and coworkers were able to extract Cu^{2+} with salicylaldoxime substituted on the imidazolium cations **(12)**;[162] in addition, they used ethylaminodiacetic acid present as di-*t*-butyl ester on the cation **(13)** which was able to extract Cu^{2+} from basic aqueous solutions.[163,164] Barber used an amidoxime-functionalized ionic liquids for the extraction of uranyl via η_2-coordination.[165] Another possibility is the **functionalization of the IL anion** with functional groups that show a certain affinity to a particular metal species. Advantageous is that these anions can be combined with hydrophobic cations and thus enhancing both selectively and efficiency of the extraction agent.[92] Kogelnig et al. synthesized anion-functionalized ionic liquids from tricaprylmethylammonium chloride (Aliquat®336) and selected Brønsted acids with thiosalicylate **(14)**, benzoate **(15)** and heaxanoate **(16)** as conjugated base.[166] These ionic liquids were then evaluated for the extraction behavior of cadmium, alkaline and earth alkaline metals. The thiosalicylate-based IL showed a very high extraction efficiency for cadmium (> 99.9 %). Rajendran investigated

the extraction behavior of heavy metal ions (Zn^{2+}, Cu^{2+}, Ni^{2+}, Fe^{3+}, Pb^{2+}) to trimethylcaprylammonium in combination with salicylate **(17)**, benzoate and anthranilate **(18)** anions.[167] Egorov et al. synthesized trimethylcaprylammonium salicylate for the extraction of Ni^{2+}, Mn^{2+}, Cu^{2+}, Fe^{2+}.[168] Mehdi et al. used 1-butyl-3-methylimidazolium hexafluoroacetylacetonate **(19)** for the extraction of Nd^{3+}, Cu^{2+} and Co^{2+}.[169]

Sun et al. introduced a new concept for the enhancement of extraction efficiencies by using *bifunctional ionic liquids* (bif-ILs). These ionic liquids are compiled from two exisiting extractants as precursor for which an enhanced synergistic extraction is found compared with the use of individual extractant precursors. In particular synergistic effects were found for the ionic liquid tricaprylmethylammonium cation combined with *sec*-octhylphenoxy acetate **(20)** for the extraction of cobalt and nickel in comparison with their analogous precursor mixture.[170] Similarly Liu used (Cyphos®IL 104) a combination of trihexyl(tetradecyl)phosphonium with bis-(2,44-trimethylpentyl)phosphinate **(21)** in soybean oil methyl ester and biodiesels as dilutant for rare earth extraction.[171] Figure 1.11 and Figure 1.12 show extractant functionalized cations and anions respectively used for the metal ion extraction.

Use of extractant functionalized ionic liquids in metal ion extraction show some promising perspectives; nevertheless, further comprehension about the extraction mechanism, complex formation as well as the influence of the physical properties on the extraction process and knowledge about the biodegradability and toxicity is necessary for the evaluation of *extractant functionalized* ionic liquids in extraction processes.[92]

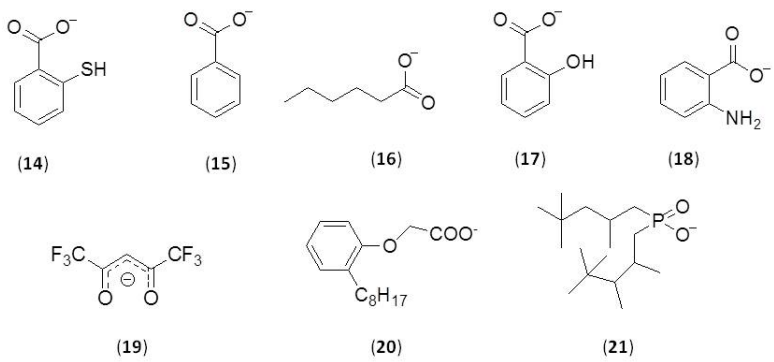

Figure 1.12: Selected *extractant functionalized* anions used for metal ion extraction to ionic liquids.

Without added extractants

Less explored are the extraction of metals with inorganic extractants. Visser et al. showed that the use of inorganic extractants such as (halides, CN^-, OCN^-, SCN^-) in ionic liquids are a feasible alternative to organic extractants because of their high D_M values; however more investigation was necessary to elucidate the nature of the extracted species and to observe whether ion exchange took place.[127] Kozonoi et al. reported the extraction of La^{3+}, Na^+, Li^+, Cs^+ , Ca^{2+}, Sr^{2+} from aqueous solution to [$C_x$mim][NfO] without using extractants.[172] They prevailed that these metals were extracted mainly via cation exchange and partial transfer of non-charged species based on the following foundings:

- Cations with large hydrated radii were more effectively extracted into the ionic liquid phase.
- The extractions of La^{3+} to [$C_x$mim][NfO] decreased with increasing nitric acid concentration and with increased hydrophobicity of the ionic liquid cation.
- The amount of La^{3+} transferred to the ionic liquid phase increases linearly with [$C_x$mim] transferred to aqueous phase, and the slope of the linear plot was almost 2.

Germani et al. reported the complete partitioning of Hg^{2+} to [$C_x$mim][PF_6] (with x = 4,6,8) in which only the alkyl chain length was adapted.[173] Papaiconomou et al. extracted gold as a tetrachlororaurate(III) complex to 1-octyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, and further platinum as a hexathiocyanatoplatinate(IV) complex in the presence of KSCN to 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, unfortunately the mechanism and the back extraction behavior is not discussed in the paper.[174] de los Rios et al. used ionic liquids based on 1-butyl-3-metylimidazolium and 1-octyl-3-metylimidazolium in combination with tetrafluoroborate, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anions and further Aliquat®336 for the extraction of Zn^{2+}, Cd^{2+} and Fe^{3+} present as halide salts in the aqueous phase to the IL phase and investigate the effect of ionic liquid composition and metal ion concentration on the extraction behavior.[175] They found Aliquat®336 to be an outstanding ionic liquid for the extraction of the metal ions, regrettably the extraction mechanism was not investigated.

All previous examples together show that metal ions can be extracted as cationic, uncharged and anionic species. The extraction mechanism of the metal ions to the ionic liquid phase appeared to be strongly dependent on the nature of the metal ion species, the aqueous electrolyte concentration, type of electrolyte and type of ionic liquid.

1.2.3 Additional remarks

The use of ionic liquids in *liquid-liquid micro-extraction* (LLME) for the concentration of trace components and the extraction of metal ions to immobilized ionic liquids such as *supported liquid membranes* (SLMs) and *polymer inclusion membranes* (PIMs) are not discussed in this thesis, although these techniques are closely related to solvent extraction the discussion will bring us beyond the scope of this dissertation. Further information about the micro extraction of metal ions can be found in the review of Hiramaya.[91] Immobilized ionic liquids are reviewed by Stojanovic et al., Cserjesi et al. and Popov et al.[19,92,96] The applications of metal extraction to ionic liquids that makes use of an added organic diluent is not discussed. The use of ionic liquids diluted in a solvent has been known since 1966[176] and more important in these applications is that the main advantages of ionic liquids, i.e. low volatility and low flammability are lost when a mixture with volatile organic solvents is used. Metal extraction in ionic liquids diluted by organic solvents are largely discussed by Stojanovic et al.[177]

In general, aqueous solutions are used as media for the electrowinning of metals such as copper, zinc, nickel and gold. However, it is not possible to deposit all metals from an aqueous phase. Metals, such as aluminium, titanium, tantalum, niobium and molybdenum with low redox potentials cannot be deposited from aqueous solutions due to the hydrolysis by water. Because ionic liquids possess excellent features such as a large electrochemical window, reasonable conductivity, transport properties and solubility of metal salts;[3,78] they might be used as an alternative media for the electrowinning of reactive metals. A broader discussion about this topic has been given in the book *Electrodeposition from ionic liquids*.[17]

1.3 Objectives

Ionic liquids are solvents that are different from water, organic solvents and molten salts. They can induce other behaviour of metal ions in solution that gives rise to specific opportunities in the processing of metals. The main objective of this thesis is to investigate the suitability of ionic liquids as solvents in metal processing, in particular for the dissolution of metal oxides and as extraction media for the separation of metals by solvent extraction. In this thesis we will mainly focus on the metals cobalt and nickel, but also other base metals, such as manganese, iron, zinc, calcium and copper will pass in review since they are of significant importance in the cobalt-nickel metallurgy.

The previous section has shown that only very little work has been done on the digestion of metal oxides in ionic liquids. This thesis aims to extend this research, which will be achieved by investigating the dissolution mechanism and the metal species in solution after the reaction of selected metal oxides in ionic liquids. Furthermore, the addition of oxide-binding reagents such as acids to ionic liquids will be examined, as this could promote metal oxide dissolution and enable direct processing of metals in ionic liquids.

The discussed literature about the application of ionic liquids in solvent extraction as extraction media for metal ions already showed that ionic liquids can extract several metals such as rare earths, actinides or base metals. However, the emphasis layed on the use of fluorinated ionic liquids, but ionic liquids with fluorinated anions are not ideal for use in solvent extraction processes, both from an economic and an environmental point of view. Furthermore, while the literature extensively studied the extraction behaviour and the mechanisms of extraction of the metal, these investigations were not aimed at achieving a separation between similar metals. This doctorate specifically aims to obtain a separation between metals, in particular cobalt and nickel, by solvent extraction using ionic liquids as extraction media. This objective will be achieved by selection of suitable non-fluorinated hydrophobic ionic liquids and by handling the practical problems that are associated with the ion exchange issue.

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CHAPTER

2

AN ENVIRONMENTALLY FRIENDLIER APPROACH TO HYDROMETALLURGY

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PAPER

An environmentally friendlier approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids

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A green solvent extraction process for the separation of cobalt from nickel, magnesium and calcium in chloride medium was developed, using undiluted phosphonium-based ionic liquids as extractants. Cobalt was extracted to the ionic liquid phase as the tetrachlorocobaltate(II) complex, leaving behind nickel, magnesium and calcium in the aqueous phase. Manganese is interfering in the separation process. The main advantage of this ionic liquid extraction process is that no organic diluents have to be added to the organic phase, so that the use of volatile organic compounds can be avoided. Separation factors higher than 50 000 were observed for the cobalt/nickel separation from 8 M HCl solution. After extraction, cobalt can easily be stripped using water and the ionic liquid can be reused as extractant, so that a continuous extraction process is possible. Up to 35 g L^{-1} of cobalt can be extracted to the ionic liquid phase, while still having a distribution coefficient higher than 100. Instead of hydrochloric acid, sodium chloride can be used as a chloride source. The extraction process has been upscaled to batch processes using 250 mL of ionic liquid. Tri(hexyl)tetradecylphosphonium chloride, tri(butyl)-tetradecylphosphonium chloride, tetra(octyl)phosphonium bromide, tri(hexyl)tetradecylphosphonium bromide and Aliquat 336 have been tested for their performance to extract cobalt from an aqueous chloride phase to an ionic liquid phase. Tri(hexyl)tetradecylphosphonium chloride (Cyphos IL 101) turned out to be the best option as the ionic liquid phase, compromising between commercial availability, separation characteristics and easiness to handle the ionic liquid.

Introduction

Liquid–liquid extraction (solvent extraction) is a very important technique for metal ion separations, both on a laboratory scale (sample preparation prior to chemical analysis) and on an industrial scale (hydrometallurgical processes for extraction and purification of metals).[1–4] Solvent extraction offers several advantages over competing techniques, such as ion-exchange processes. Advantages include the ability to operate in a continuous mode, to employ only relatively simple equipment and small quantities of reagents, and to achieve a high sample throughput. The method is very flexible because the extraction process can be tailored by a suitable choice of the process parameters, *e.g.*, the nature and concentration of the extractants, the composition of the aqueous and organic phase, *etc.* The traditional liquid–liquid extraction process makes use of water-immiscible organic solvents, many of which are flammable, volatile or toxic. Examples of solvents are kerosene, dodecane, toluene, dichloromethane, chloroform and diethyl ether. The growing awareness of safety and environmental impact related with the use of these organic solvents renders their replacement with less noxious alternatives desirable. There is presently an increasing research activity in the field of the development of sustainable separation processes, including those based on ionic liquids.[5–10] Ionic liquids (ILs) are solvents that consist entirely of ions.[11–14] Typically, they are organic salts with a melting point below 100 °C. Major advantages of ionic liquids for application in solvent extraction processes are their low volatility and low flammability. In 1998, Rogers and co-workers were the first to suggest that ionic liquids may be suitable as the basis for novel liquid–liquid extraction processes.[15] They demonstrated that a variety of ionisable and non-ionisable aromatic molecules are transferred from water into the ionic liquid [C_6mim][PF_6], with distribution ratios of more than 1000 in some cases, *e.g.*, for the extraction of 4,4′-dichlorobiphenyl.

Although ionic liquids have proved to be interesting and useful solvents for the extraction of neutral organic compounds, including natural products, the high expectations have only been partially met in the case of application of ionic liquids for solvent extraction of metal ions. First of all, the transfer of hydrated metal ions from an aqueous phase to a hydrophobic ionic liquid phase is unfavourable, so that extractants have to be

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used. The mechanisms for extraction of metal ions into ionic liquids are in many cases different from what is observed for extraction into molecular solvents. The main problem is that extraction of metal ions from an aqueous phase into an ionic liquid phase often takes place *via* an ion-exchange mechanism.[16,17] This means that upon extraction ionic liquid components are solubilised in the aqueous phase. Ionic liquid cations are lost during extraction of a metal ion with a neutral extractant such as a crown ether, whereas ionic liquid anions can be lost during extraction of anionic metal complexes. These losses of ionic liquid by solubilisation in the aqueous phase are a serious problem that hampers the general application of ionic liquids for liquid–liquid extraction processes.[18] Although these losses of ionic liquid can be reduced by structural variation of the ionic liquid, *e.g.*, by increasing the alkyl chain length or fluorination of the alkyl chain, these modifications often have a negative effect on the distribution ratios and the extraction efficiency.[19] Because water-immiscible ionic liquids are required for solvent extraction, the choice of the ionic liquid is limited to hydrophobic ionic liquids.[20] These ionic liquids often contain fluorinated anions, such as the hexafluorophosphate (PF_6^-) or the bis (trifluoromethylsulfonyl)imide (Tf_2N^-) anion.[21] Fluorinated ionic liquids are quite expensive, so that the use of ionic liquids for classic solvent extraction processes cannot be justified from an economical point of view, especially not because the advantages of ionic liquids for these applications are limited to their low volatility and flammability. Moreover, there are concerns about the toxicity of these ionic liquids and hexafluorophosphate anions are not stable against hydrolysis.[22] Examples of non-fluorinated ionic liquids that are not miscible with water are Aliquat 336[23] and tri(hexyl)tetradecylphosphonium chloride (Cyphos® IL 101).[24] Although these ionic liquids have been used in solvent extraction studies of metal ions, they are never applied in a pure state, but they are dissolved in diluents such as toluene or kerosene.[25–31] The diluents largely decrease the viscosity of the organic phase and thus accelerate the kinetics of the solvent extraction process, but the diluents are also volatile organic solvents. Therefore, the advantages of using ionic liquids for solvent extraction are lost. The diluents can be omitted by impregnating a solid support with the ionic liquid, but this practice has often a negative effect on the capacity of the ionic liquid for separation of metal ions.[32,33] Ionic liquids with non-fluorinated anions have also been used for the dissolution of metal oxides or for the leaching of metals from ores or industrial waste products.[34–39]

In this paper, we show that an efficient solvent extraction process for the separation of cobalt and nickel from a chloride medium can be developed by using phosphonium ionic liquids. The separation of cobalt and nickel by solvent extraction is an important industrial hydrometallurgical process.[40–49] In our method, the phosphonium ionic liquid acts as an undiluted extractant. No addition of volatile organic solvents to the organic phase is required. The optimum extraction parameters have been determined. With separation factors higher than 50 000, this solvent extraction process is more efficient than industrial processes currently in use. The process has been scaled up to 250 mL batches of ionic liquid. Attention has been paid to the stripping of cobalt from the ionic liquid phase and to the recycling of the ionic liquid.

Experimental

Chemicals

Tri(hexyl)tetradecylphosphonium chloride (>97%) (Cyphos® IL 101) was purchased from Cytec Industries Inc. (Niagara Falls, Ontario, Canada). Tri(butyl)tetradecylphosphonium chloride (>95%), tetra(octyl)phosphonium bromide, tri(hexyl)tetradecylphosphonium bromide were purchased from IoLiTec (Heilbronn, Germany) and Aliquat 336 was obtained from Fluka (Sigma-Aldrich Co, Bornem, Belgium). $CoCl_2{\cdot}6H_2O$ (>97%), $MnCl_2{\cdot}4H_2O$ (>99%) and $MgCl_2{\cdot}6H_2O$ (>99%) were purchased from Merck (Overijse, Belgium), $NiCl_2{\cdot}6H_2O$ (>99%) and $CaCl_2{\cdot}2H_2O$ (>98%) were purchased from VWR (Leuven, Belgium). Hydrochloride solutions were prepared from HCl (Selectipur VLSI, 36% BASF) and demineralised water. Potassium oxalate monohydrate was purchased from ACROS Organics (Geel, Belgium). All chemicals were used as received, without further purification.

Instrumentation and analysis methods

The water content of the ionic liquid after the extraction was determined with a Mettler Toledo DL 39 Karl Fischer Coulometer. The viscosity was measured using a falling ball type viscosimeter (Gilmont Instruments). Absorption spectra were measured with a Varian Cary 5000 spectrophotometer. A quartz cuvette with an optical path length of 0.1 mm was used. The HCl concentration of the organic phases after extraction was determined by a titration method. A solution of potassium oxalate (0.15 M, 100 mL) was prepared. An additional portion of 2 g of solid potassium oxalate was added to ensure an excess of oxalate. The solution was stirred and the pH was adjusted to a value of 5.75 to 6 with HCl (1 N). The solution of the sample (1 mL) was added to the oxalate solution to avoid precipitation of $Co(OH)_2$ and titrated with sodium hydroxide (0.2 N) until the original pH value was reached. The metal contents of the aqueous and organic phases after extraction for the lab scale experiments were determined using a bench top total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). For analysis of the aqueous phase by TXRF, aqueous samples (1 mL) were measured after addition of gallium as an internal standard. The samples were diluted with MilliQ50 water (if necessary). A small aliquot of 10 μL (solution) was applied on a quartz glass carrier, dried by evaporation in a hot air oven (80 °C) and measured with a measurement time of 200 s. For the determination of the metal content in an organic phase by TXRF, a certain weight of the extracted phase (±0.5 g) was diluted in dioxane (20 mL). Gallium was added to the solution as an internal standard. A small aliquot of 5 μL solution was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 400 s. The metal contents of the aqueous and organic phases after extraction for the batch scale experiments were determined using ICP-OES (Varian Vista Pro). For analysis of the aqueous phase by ICP-OES, the samples were diluted in 10 vol.% HCl. A calibration curve was prepared for the concentration range for 0–10 mg L^{-1} and scandium was used as an internal standard. The spectra were measured with a power of 1.4 kW, an argon

flow of 15 L min^{-1} and an auxiliary flow (Ar) of 1.5 L min^{-1}. For analysis of the organic phase by ICP-OES, the organic samples were decomposed with a mixture of H_2SO_4 and HNO_3 in a quartz beaker on a heating plate. H_2SO_4 and HNO_3 were evaporated and the residue was dissolved in 10 vol.% HCl before measurement as described for aqueous solutions. The total carbon content (TOC) was measured using a Shimadzu TOC-VWP TOC analyzer. The organic carbon was converted to CO_2 by addition of an oxidizing acidic solution (60 g of $Na_2S_2O_8$ and 15 mL of H_3PO_4 (85%) in 500 mL of water) in a heated UV reactor (80 °C). The formed CO_2 was carried *via* a carrier gas flow (N_2, 200 mL) to a non-dispersive infrared detector, where CO_2 was measured. A calibration curve was prepared to relate the detector signal to the CO_2 concentration and hence to the corresponding carbon concentration of the sample.

Small-scale extraction experiments

To determine the distribution coefficients as a function of the cobalt concentration present in the feed solution, an aqueous solution of Co(II) with a hydrochloric acid content of 8 M containing $CoCl_2{\cdot}6H_2O$ with the desired metal concentration (5 to 50 g L^{-1}) was prepared and tri(hexyl)tetradecylphosphonium chloride was used as extraction phase. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The cobalt concentration in the aqueous phase was analysed. For the extraction at a 4 M sodium chloride concentration, an aqueous solution containing $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ (at a concentration of 5 g L^{-1}) and with a NaCl content of 4 M was prepared. Tri(hexyl)tetradecylphosphonium chloride was used as the extraction phase. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The metal content of both phases was analysed after centrifugation (3000 rpm, 10 min). To test the performance of the ionic liquids tri(butyl)tetradecylphosphonium chloride, tetra(octyl)phosphonium chloride, tri(hexyl)tetradecyl phosphonium bromide and Aliquat 336 for the extraction of cobalt and nickel, an aqueous 8 M HCl solution containing $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ (with a metal concentration of 5 g L^{-1}) was prepared. 5 mL of the aqueous solution and 5 mL of the ionic liquid phase were stirred for 10 min at 60 °C. The metal content of both phases was analysed after centrifugation (3000 rpm, 10 min).

Batch-scale extraction experiments

Extraction batch test 1: An aqueous solution of Co(II) and Ni(II) with a metal concentration of 5 g L^{-1} was prepared from $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ in 8 M HCl. The aqueous solution (250 mL) was poured in a jacketed reactor vessel (500 mL) and the liquid extraction reagents tri(hexyl)tetradecylphosphonium chloride (250 mL) was added. After intensively stirring at 1040 rpm for 10 min at 60 °C, equilibrium was reached and the phases were allowed to settle. Both phases were analyzed for their metal content after centrifugation (3000 rpm, 10 min).

Extraction batch test 2: An aqueous solution of 8 M HCl (250 mL) was poured in a jacketed reactor vessel (500 mL) and the ionic liquid extractant tri(hexyl)tetradecylphosphonium chloride (250 mL) was added. Equilibrium was reached after intensively stirring at 1040 rpm for 10 min at 60 °C and the phases were allowed to settle. After phase separation, the organic phase (now loaded with water and hydrochloride) was reused as extraction phase and an extraction was performed, as described for extraction batch test 1 (see above). The metal content of the two phases was analysed after centrifugation (3000 rpm, 10 min).

Extraction batch test 3: An aqueous 8 M HCl solution containing $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $CaCl_2{\cdot}2H_2O$, and $MgCl_2{\cdot}6H_2O$ with a metal concentration of 5 g L^{-1} was prepared. The aqueous solution (500 mL) was poured in a jacketed reactor vessel (1 L) and the extraction phase tri(hexyl)tetradecylphosphonium chloride (500 mL) was added. Equilibrium was reached after intensively stirring at 1040 rpm for 10 min at 60 °C and the phases were allowed to settle. The metal content of the two phases was analysed after centrifugation (3000 rpm, 10 min).

Stripping conditions: Water (40 mL) as the stripping phase was poured in a jacketed reactor vessel (250 mL), and the extraction phase from extraction batch test 2 containing Co(II) (circa 5 g L^{-1}, 80 mL) was added. After intensive stirring at 1040 rpm for 10 min at 60 °C, the phases were allowed to settle. The cobalt concentration in the aqueous phase was measured after centrifugation (3000 rpm, 10 min). The organic phase was recycled after each stripping step and reused until no residual cobalt could be detected in the ionic liquid phase.

Distribution coefficients and separation factor

The distribution coefficient for cobalt D_{Co} was calculated as follows:

$$D_{Co} = \frac{[Co]_0 - [Co]_{aq}}{[Co]_{aq}} \quad (1)$$

where $[Co]_0$ is the initial cobalt concentration in the aqueous phase before extraction and $[Co]_{aq}$ is the cobalt concentration in the aqueous phase after the extraction. Distribution coefficient for nickel D_{Ni} was calculated using the following equation:

$$D_{Ni} = \frac{[Ni]_{org}}{[Ni]_0 - [Ni]_{org}} \quad (2)$$

where $[Ni]_0$ is the initial nickel concentration in the aqueous phase before extraction and $[Ni]_{org}$ is the nickel concentration in the organic phase after the extraction. The efficiency of separation of cobalt from nickel is described by the separation factor β:

$$\beta_{Ni}^{Co} = \frac{D_{Co}}{D_{Ni}} \quad (3)$$

The distribution coefficient for manganese (D_{Mn}) is defined in a way similar to that of cobalt (eqn (1)), whereas the distribution coefficients for calcium (D_{Ca}) and magnesium (D_{Mg}) were defined in a way similar to that of nickel (eqn (2)).

Results and discussion

Tri(hexyl)tetradecylphosphonium chloride (Cyphos® IL 101 or $P_{66614}Cl$) was selected for the extraction experiments with cobalt

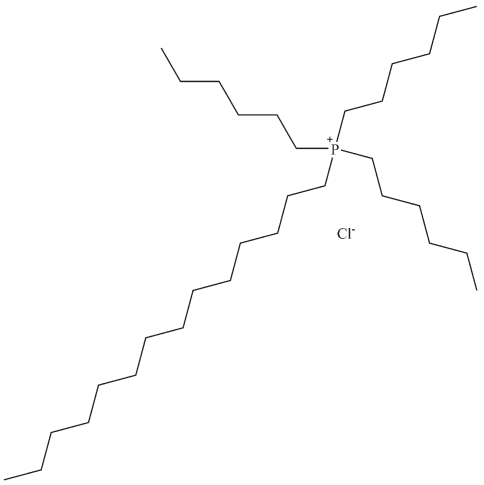

Fig. 1 Structure of tri(hexyl)tetradecylphosphonium chloride ($P_{66614}Cl$).

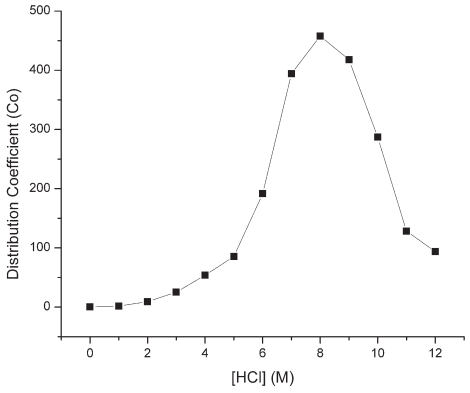

Fig. 2 Distribution coefficient of cobalt(II) as a function of the HCl concentration.

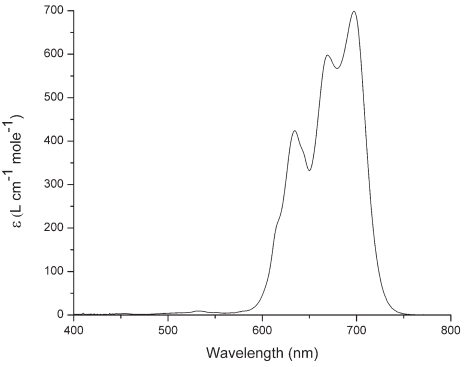

Fig. 3 Absorption spectrum of the ionic liquid phase after extraction, containing bis(tri(hexyl)tetradecylphosphonium) tetrachlorocobaltate(II). The absorption spectrum is typical for the $[CoCl_4]^{2-}$ anion.

and nickel, because it is a room-temperature ionic liquid and because it is one of the few examples of non-fluorinated ionic liquids that are largely immiscible with water (Fig. 1). Moreover, this ionic liquid is commercially available and has no surfactant properties, in contrast to quaternary ammonium and phosphonium salts with one long alkyl chain and three short alkyl chains. The absence of surfactant properties enhances the phase separation after mixing of organic and aqueous phase. Although cobalt is often extracted from sulphate medium, it was decided to switch to chloride medium to have in the aqueous and ionic liquid phase the same anion. Cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$) was used as the cobalt source, and nickel(II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$) as nickel source. Typically, the extraction experiments were performed at 60 °C to reduce the viscosity of the ionic liquid phase. Phosphonium ionic liquids are known to be very viscous at room temperature.[50,51]

In a first series of experiments, the optimal chloride concentration was determined by varying the HCl concentration of the feed solution. It was found that the extraction efficiency of cobalt increases with increasing chloride concentration, with a maximum at a chloride concentration of 8 M (Fig. 2). This decrease in efficiency of extraction of cobalt(II) at high HCl concentration has also been observed by other authors for extraction of cobalt(II) by quaternary ammonium salts.[52] This behaviour is attributed to the extraction of the excess HCl, probably in the form of the hydrogen dichloride ion, $[HCl_2]^-$.[53] The extracted cobalt(II) species is the tetrahedral tetrachlorocobaltate(II) complex, $[CoCl_4]^{2-}$. This species was identified by optical absorption spectroscopy in the aqueous phase and in the ionic liquid phase, on the basis of its typical absorption spectrum (Fig. 3). The absorption band in the visible region with different submaxima, due to the spin orbit coupling, can be assigned to the $^4T_{1g}(P) \leftarrow {}^4A_2$ transition.[54,55] The molar absorptivity ε values are in the typical range for tetrahedral cobaltate(II) complexes, with values ranging between 10^2 and 2×10^3 L cm^{-1} mole^{-1}. These absorptivity values are clearly distinct from the values for octahedral cobalt(II) complexes, which range between 5 and 40 L cm^{-1} mole^{-1} for the $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition. The $[CoCl_4]^{2-}$ ion is also found upon dissolution of anhydrous $CoCl_2$ in the ionic liquid 1-butyl-3-methylimidazolium chloride.[56] Ionic liquids with the $[CoCl_4]^{2-}$ have been described in the literature.[57,58] The extraction mechanism of cobalt to the ionic liquid phase can be described as an anion exchange mechanism, in which the $[CoCl_4]^{2-}$ complex which is present in the aqueous phase at high chloride concentrations is extracted into the ionic liquid phase. During the extraction process, for every $[CoCl_4]^{2-}$ unit extracted to the ionic liquids phase, two chloride ions are released from the ionic liquid phase to the aqueous phase:

$$[CoCl_4]^{2-} + 2\overline{[P_{66614}]Cl} \rightarrow \overline{[P_{66614}]_2[CoCl_4]} + 2Cl^- \quad (4)$$

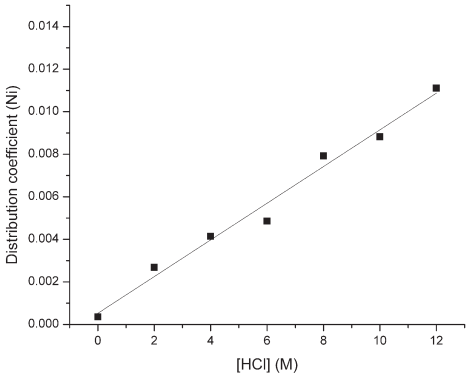

Fig. 4 Distribution coefficient of nickel(II) as a function of the HCl concentration.

Table 1 Results of the extraction after extraction batch tests 1 and 2

	Batch test 1	Batch test 2[a]
$[Co]_{aq}$ (mg L^{-1})	11 (±0.5)	14 (±1.4)
$[Ni]_{org}$ (mg L^{-1})	44 (±2.7)	43 (±3.6)
D_{Co}	460 (±21)	360 (±32)
D_{Ni}	0.0088 (±0.0006)	0.0087 (±0.0007)
β_{Ni}^{Co}	52 000 (±2800)	41 000 (±3300)

[a] Using an ionic liquid phase, saturated with water and HCl.

where the bars denote species in the organic (ionic liquid) phase. The extraction efficiency of nickel(II) linearly increases with increasing chloride concentration, but the absolute values of the distribution coefficient remain low (Fig. 4). The highest selectivity between cobalt and nickel was obtained at 8 M HCl concentration.

A batch extraction experiment with 250 mL of ionic liquid was performed with an aqueous 8 M HCl solution containing a mixture of cobalt and nickel (both at 5 g L^{-1}) (*extraction batch test 1*). The cobalt concentration in the aqueous phase, nickel concentration in the organic phase after extraction, the distribution coefficients and separation factor are given in Table 1. The data show that cobalt is preferentially extracted to the ionic liquid phase, while nickel remains in the aqueous phase. When the physical properties of the ionic liquid phase are compared before and after extraction (Table 2), it can be concluded that water and hydrochloric acid are partly co-extracted to the ionic liquid phase. This can be explained by the ionic nature of the ionic liquid, which attracts water molecules to their surroundings (solvation shell). The absorption of water by the ionic liquid is responsible for the sharp decrease in viscosity (from 280 to 101 cP at 60 °C) and makes the ionic liquid phase much easier to handle during the extraction process. Due to the extraction of water and HCl to the ionic liquid phase, the volume of the aqueous phase decreases. This change in volume can easily be prevented by saturating the ionic liquid with water and HCl before the extraction reaction. In *extraction batch test 2*, the ionic liquid phase was equilibrated by a 8 M HCl solution before the start of the extraction experiment (Fig. 5, Table 1). It should be realized that also in a continuous extraction process, the ionic liquid phase will be saturated by the acidic water solution. The physical properties of the ionic liquid before and after extraction are presented in Table 3. By using an ionic liquid phase saturated by the aqueous 8 M HCl solution, the ratio of the volumes of the aqueous and the ionic liquid phase remains constant. When these results are compared with the results of extraction batch test 1 (Table 1), a decrease in the distribution coefficients of cobalt is observed. Because ±15 wt% less ionic liquid is present due to the absorption of water and HCl (±15 wt%), the concentration ratio between the ionic liquid and cobalt present in the feed solution decreases. This situation is actually the same as having 15% more cobalt in the feed solution. An experiment with 15% extra cobalt in the feed solution was carried out and this led to the same results. This result also agrees with the observation that the distribution coefficient decreases with increasing cobalt concentrations in the feed solution (see further).

Table 2 Physical properties of the ionic liquid before and after extraction batch test 1 (at 60 °C)

	Before extraction	After extraction
Water content (wt%)	0.1	7.7
HCl content (wt%)	0	5.2
Viscosity (cP)	280	101
Density (g mL^{-1})	0.87	0.91
Phase separation time (s)	—	90

When the extraction is performed with an aqueous feed solution containing besides cobalt and nickel also manganese, magnesium and calcium (*extraction batch test 3*), no good separation of cobalt and manganese could be obtained. Manganese is co-extracted together with cobalt. Magnesium, calcium and nickel remain in the aqueous phase and can thus be separated from cobalt and manganese. To end up with a pure cobalt solution, manganese needs to be removed from the aqueous feed before the extraction step. Distribution coefficients for cobalt and the other elements are given in Table 4. Due to the higher viscosity of ionic liquids, compared to classical organic solvents, entrainment of ionic liquid in the water phase can be an issue. A higher viscosity can hinder the phase separation during settling. Loss of ionic liquid in the water phase needs to be avoided because of ecological and economic reasons. The total organic content was measured in the aqueous phase after extraction. The data show that only very small quantities of the ionic liquid are lost towards the aqueous phase. For instance, the concentration of the ionic liquid in the aqueous phase after extraction was only 4.2 mg L^{-1} for extraction batch test 1, <40 mg L^{-1} for extraction batch 2 and 11 mg L^{-1} for extraction batch test 3. Cobalt can be stripped from the ionic liquid phase by water. Four steps are required to strip the total cobalt content of the ionic liquid. The percentage of cobalt stripped from the ionic liquid is reported in Table 5. The stripping of cobalt is possible because water will wash the excess of chlorides from the ionic liquid phase, leading to transformation of the tetrachlorocobaltate(II) complex to the hexaaquocobalt(II) complex. After four stripping steps, no HCl remains in the ionic liquid phase and the ionic liquid phase

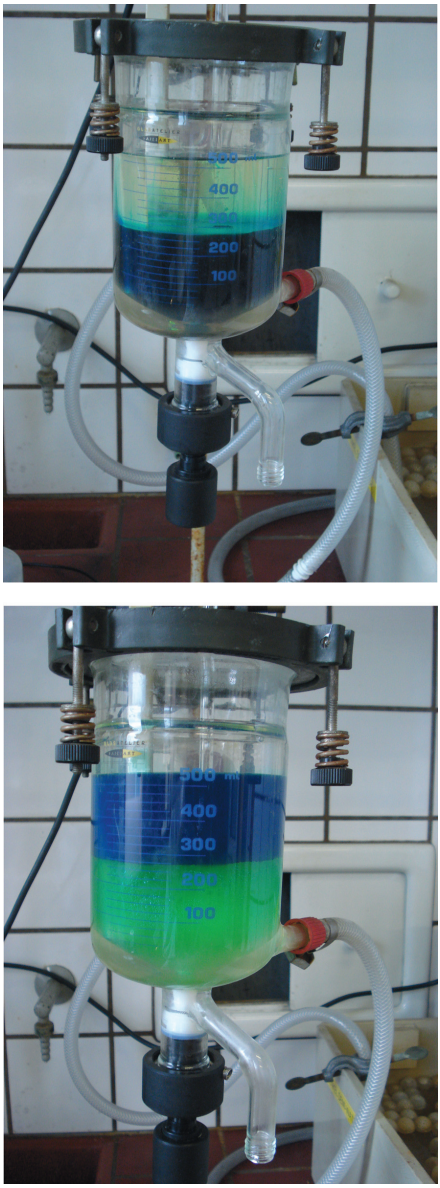

Fig. 5 Top: batch scale reactor before extraction batch test 2. Bottom: batch scale reactor after extraction batch test 2; (upper phase = ionic liquid). It is can be observed that cobalt(II) is extracted as the dark blue tetracobaltate(II) complex to the ionic liquid phase, while the green hydrated nickel(II) ions remains in the aqueous phase.

contains 15 wt% of water. This ionic liquid phase can be reused to extract a new load of cobalt from an aqueous solution. An additional purification step can be done by scrubbing the ionic liquid phase with an aqueous solution of 8 M HCl to remove co-extracted nickel from the ionic liquid phase.

Table 3 Physical properties of the ionic liquid before and after extraction batch test 2, using an ionic liquid phase, saturated with water and HCl

	Before extraction	After extraction
Water content (wt%)	8.7	6.9
HCl content (wt%)	6.0	5.8
Viscosity (cP)	95	101
Density (g mL^{-1})	0.90	0.91
Phase separation time (s)	—	90

Table 4 Distribution coefficients *D* for cobalt(II), nickel(II), manganese(II), magnesium(II), and calcium(II)

Element	*D*
Co	450
Ni	0.0062
Mn	30
Mg	0.0014
Ca	0.0056

Table 5 Percentage of cobalt that is stripped to aqueous phase

Stripping step	Amount of cobalt stripped (%)
1	2.5
2	28
3	52
4	17.5
Total	100

The theoretical cobalt loading capacity of the ionic liquid is 50 g L^{-1}. In this case, all the chloride anions of the ionic liquid phase are completely converted into the tetrachlorocobaltate(II) anion. To compensate the double negative charge of this anion, two phosphonium cations are required. At higher cobalt concentrations longer stirring times are needed to reach equilibrium. This is shown in Fig. 6 where the distribution coefficient of cobalt was plotted as a function of stirring time when a feed solution of 30 g L^{-1} cobalt was used. The fact that longer stirring times are required can be explained by the increased viscosity due to higher cobalt concentration in the ionic liquid phase. The increase in viscosity with increasing cobalt concentration is shown in Fig. 7. To determine the distribution coefficients as a function of the cobalt concentration the following stirring times were used: 10, 20, 60 and 120 min respectively for cobalt concentrations of 5–15 g L^{-1}, 20–25 g L^{-1}, 30 g L^{-1}, 35–50 g L^{-1}. When the distribution coefficient of cobalt is plotted as a function of the cobalt concentration of the aqueous feed, the distribution coefficient of cobalt decreases with increasing cobalt concentration of the feed solution (Fig. 8). Since cobalt is present as the $[CoCl_4]^{2-}$ complex, more tetrachlorocobaltate(II) is loaded on the organic phase upon extraction. Because double charges have higher repulsive forces to each other than single charges there are more repulsive forces built up in the ionic

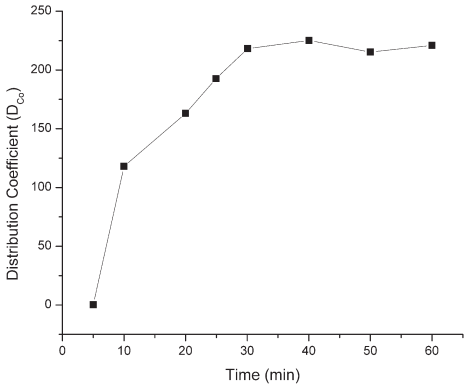

Fig. 6 Distribution function of cobalt as a function of time for a feed solution of 30 g L^{-1} cobalt.

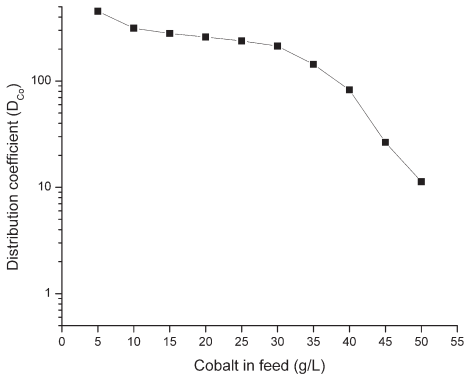

Fig. 8 Distribution coefficient as a function of the cobalt concentration in the aqueous feed solution.

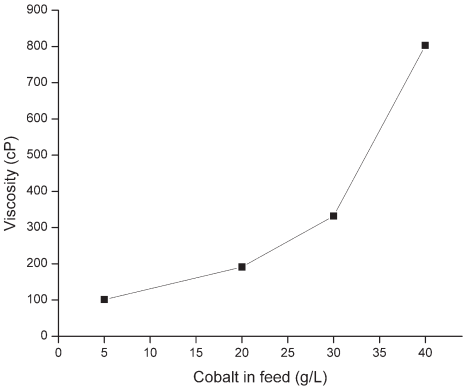

Fig. 7 Viscosity of the ionic liquid phase after extraction at 60 °C as function of cobalt concentration in the feed solution.

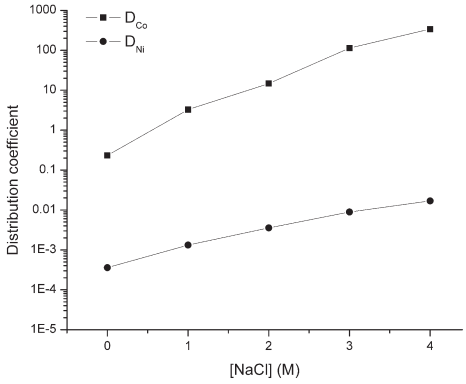

Fig. 9 Distribution coefficient of cobalt and nickel as a function of the sodium chloride concentration.

liquid phase This will result in displacement of the doubly charged tetrachlorocobaltate(II) complex from the ionic liquid.

Other chloride sources instead of hydrochloric acid can be used for the selective extractions of cobalt. Another extraction was performed using sodium chloride as chloride source. First the optimal chloride concentration was determined by varying the NaCl concentration of the feed solution. At higher concentrations (5 M) sodium chloride is precipitating in the aqueous phase upon extraction. It was found that the extraction efficiency of cobalt and nickel are increasing with increasing chloride concentration. (Fig. 9). The highest separation for cobalt over nickel could be obtained with a concentration of 4 M NaCl. This is a quite low chloride concentration compared to the extraction with the feed solutions saturated by 8 M HCl. The reason for this can be found in the salting out effect. By using sodium chloride as chloride source, nickel will be pushed to the ionic liquid phase, but to a much lower extent than cobalt. A good separation of cobalt and nickel can still be obtained under these conditions. In Table 6 the extraction results using sodium chloride are shown. The advantage of using sodium chloride solutions over hydrochloric acid solution is that they are less aggressive media, cheaper and lower concentrations of chloride are needed.

Other phosphonium based ionic liquids can be used as extraction phases provided that they are largely immiscible with the aqueous phase. Three other phosphonium ionic liquids were tested for their extraction characteristics: tetra(octyl)phosphonium bromide ($P_{8888}Br$) and tri(butyl)tetradecylphosphonium chloride ($P_{44414}Cl$) and tri(hexyl)tetradecylphosphonium bromide ($P_{66614}Br$). These phosphonium ionic liquids were selected because of their hydrophobic nature and commercial availability. A disadvantage of the ionic liquids $P_{8888}Cl$ and $P_{44414}Cl$ is that they are solid at room temperature and are therefore more difficult to handle. The ionic liquid $P_{66614}Br$, where the chloride anion from Cyphos IL 101 is replaced with bromide, is liquid at room temperature. The results of the

Table 6 Extraction results for extraction of cobalt and nickel from aqueous feed solutions containing 4 M NaCl to tri(hexyl)-tetradecylphosphonium chloride

$[Co]_{aq}$ (mg L^{-1})	21 (±3)
$[Ni]_{org}$ (mg L^{-1})	98 (±4.6)
D_{Co}	240 (±29)
D_{Ni}	0.020 (±0.0010)
β_{Ni}^{Co}	12 000 (±1000)

Table 7 Extraction results for the separation of cobalt and nickel using different ionic liquids as the extractant phase

	$P_{8888}Br$	$P_{44414}Cl$	$P_{66614}Br$	$P_{66614}Cl$
$[Co]_{aq}$ (mg L^{-1})	11	180	11	11
$[Ni]_{org}$ (mg L^{-1})	23	300	39	44
D_{Co}	450	27	450	460
D_{Ni}	0.0046	0.064	0.0078	0.0088
β_{Ni}^{Co}	98 000	420	58 000	52 000
Water content of IL after extraction (%)	3.8	23.4	7.3	7.7

phosphonium extraction phase were compared with those of tri-(hexyl)tetradecylphosphonium chloride. From the results given in Table 7, when using $P_{8888}Br$ as the extraction phase, a separation factor of nearly 10^5 is achieved. When the water content in the organic phase is measured after extraction (Table 7), less water is extracted to the ionic liquid phase and less nickel ends up in the ionic liquid phase. $P_{8888}Br$ is a less polar ionic liquid, and therefore its hydrophobicity increases, leading to a lower uptake of water and better separation efficiency. When $P_{44414}Cl$ is used as the extraction phase poor separation efficiency for cobalt over nickel was observed compared to $P_{66614}Cl$. The separation factor is 10^2 times lower. When the water content is measured after extraction, 23.4 wt% of water is extracted to the ionic liquid phase. The extraction of water is responsible for the decrease in separation efficiency between cobalt and nickel. With increasing water content more nickel was found in the ionic liquid phase and cobalt is extracted in a lower extend to the ionic liquid phase when less hydrophobic ionic liquids are used. With the third phosphonium ionic liquid, $P_{66614}Br$, the extraction results are comparable to these of $P_{66614}Cl$. Likewise the water content in the ionic liquid phase after extraction are comparable. However, for the industrial application of this process it is better to use the chloride ionic liquid because the ionic liquid can easily be generated after extraction, with the bromide ionic liquid this is much more difficult. In general other phosphonium ionic liquids could be used as extraction phase for the separation of cobalt from nickel. Enhanced extraction results are expected with increasing hydrophobicity. The performance of the phosphonium chloride Cyphos IL 101 and an ammonium ionic liquid Aliquat 336 as extraction phase for the separation of cobalt from nickel were compared. Both ionic liquids are commercially available. Recently, the nitrate version of Aliquat 336 has been used as the organic phase for the extraction of rare earths with the phosphine oxide extractant Cyanex 925.[59] The extraction results are shown in Table 8. When Cyphos IL 101 is used as extractant instead of Aliquat 336 at 8 M HCl, the separation factor is at least 20 times higher. Using the phosphonium ionic liquid has thus superior extraction characteristics. This can be explained by the increased hydrophobicity of the phosphonium ionic liquid.

Table 8 Extraction results after extraction using Aliquat 336 and Cyphos IL 101 as extraction phase

	Aliquat 336	Cyphos IL 101
$[Co]_{aq}$ (mg L^{-1})	60	11
$[Ni]_{org}$ (mg L^{-1})	160	44
D_{Co}	80	460
D_{Ni}	0.03	0.0088
β_{Ni}^{Co}	2500	52 000

Conclusions

Cobalt can selectively be separated from nickel, magnesium and calcium with solvent extraction using phosphonium-based ionic liquids as extraction reagents. A separation of factor of 5×10^4, 8×10^4, 3×10^5 is observed for Ni, Ca and Mg, respectively. After extraction cobalt can easily be stripped using water where four stripping steps are required to strip the total cobalt content. After stripping the ionic liquid can be reused as the extraction phase, which makes it possible to do the extraction in a continuous process. Up to 35 g L^{-1} of cobalt can be extracted to the ionic liquid phase while still having a distribution coefficient of more than 10^2. Instead of hydrochloric acid, sodium chloride can be used as a chloride source. Phosphonium ionic liquids can be made more hydrophobic by lengthening the alkyl chains so that their miscibility with water will become negligible. An advantage associated with the use of (phosphonium) ionic liquids as the extraction phase is that volatile organic compounds are avoided and this offers a greener approach to solvent extraction. By doing extractions on a batch scale set-up, the practical implementation of ionic liquid as extraction phase has been proved. Three phosphonium and one ammonium ionic liquids were compared for their extraction capabilities where tri(hexyl)-tetradecylphosphonium chloride in particular seems to be superior and the best option as ionic liquid phase as a compromise between commercial availability, separation characteristics and the ease to handle the ionic liquid. This work shows that fluorine-free ionic liquids cannot only be used for solid–liquid extraction and leaching of ores or industrial solid wastes, but also as undiluted organic phases in conventional liquid–liquid extraction for the separation of metal ions.

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CHAPTER

3

CONTINUOUS IONIC LIQUID EXTRACTION PROCESS

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A continuous ionic liquid extraction process using the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) has been developed for the selective extraction of cobalt from nickel. The performance of this continuous extraction process is competitive with that of currently applied industrial processes. Moreover, the elimination of volatile odorous compounds from the extraction phase leads to environmentally friendlier and healthier working conditions.

Introduction

Solvent extraction is one of the major hydrometallurgical techniques for the separation and purification of metals.[1] This technique has gained interest because it is possible to operate it in a continuous mode, with a high throughput and relatively simple equipment. In metal separation *via* solvent extraction a water-immiscible phase (extraction phase) is mixed with an aqueous solution containing metal ions. The metal ions are distributed between the two phases and the extraction phase is selectively enriched with one or more metals. The extraction phase contains three main components: an extractant, modifiers and a diluent. The extractant is the active species which transfers the metal ions between the two phases. Modifiers are added in order to improve the properties of the extraction phase. The diluent is an organic solvent, such as kerosene, dodecane, toluene, dichloromethane and diethyl ether, capable of dissolving the extractant. These solvents are toxic, flammable and/or volatile so that replacement of these volatile organic solvents with environmentally friendlier alternatives is a high priority, given the growing awareness of safety and environmental issues. Ionic liquids (ILs) are a possible alternative for the volatile solvents in the extraction phase, because ionic solvents are non-volatile and non-flammable.[2,3] Ionic liquids offer possibilities to make the hydrometallurgical process environmentally friendlier,[4,5] and they have been investigated intensively for the extraction of metal ions.[6–13] However, it has been shown that the ionic liquid anions and/or cations can be lost to the aqueous phase *via* an ion exchange mechanism.[14–16] This makes the practical implementation of ionic liquids in solvent extraction difficult, both from an economical and an environmental point of view. Recently, we developed a more environmentally friendlier approach for the use of ionic liquids in solvent extraction processes, by a non-fluorinated ionic liquid playing the role of both the extractant and the diluent.[17] More particularly, cobalt was selectively extracted from nickel present in an aqueous phase by using the ionic liquid trihexyl(tetradecyl)phosphonium chloride as the extraction phase, eliminating the volatile and flammable character of the extraction phase. This extraction system was also applied to the separation of iron from neodymium and of cobalt from samarium.[18] These separations are relevant to recycling of rare earths from permanent magnets.[19]

It has been stated that the use of ionic liquids without diluents in solvent extraction processes is not practical at all, because of the high viscosity of the ionic liquid phase.[20] However, in this communication, we demonstrate that a continuous solvent extraction process for the separation of cobalt from nickel is possible using ionic liquids without organic diluents and that it could be competitive with current industrially applied processes after minor optimizations. To the best of our knowledge, the use of ionic liquids without organic diluents in a continuous solvent extraction process has not been described in the literature yet.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium chloride (>97%) (Cyphos® IL 101) was purchased from Cytec Industries Inc. (Niagara Falls, Ontario, Canada). $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ (>99%) were obtained from VWR (Leuven, Belgium). Hydrochloride

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solutions were prepared from HCl (Selectipur VLSI, 36% BASF) and demineralised water. All chemicals were used as received without further purification.

Instrumentation and methods

The metal contents of the aqueous and organic phases were determined using ICP-OES (Varian Vista Pro). The chloride content was determined by potentiometric titration with $AgNO_3$. The total carbon content (TOC) was measured using a Shimadzu TOC-VWP TOC analyzer. The sample preparation has been described earlier.[17] Peristaltic pumps (Gilson minipuls 3) (P1, P2, P4) and a plunger pump (CAT Labo pump – HPLH 200) (P3) were used to pump the solutions.

Experimental set up

15 L of a synthetic aqueous feed solution of Co(II) and Ni(II) with a metal concentration of 5 g L^{-1} for both metals was prepared from $CoCl_2{\cdot}6H_2O$ and $NiCl_2{\cdot}6H_2O$ in 7.6 M HCl. The ionic liquid Cyphos® IL 101 (7 L) was presaturated with water (approximately 14 wt%) in order to keep the volume ratio of the phases constant and to decrease the viscosity of the ionic liquid phase. The ionic liquid feed was kept at a temperature of 60 °C. Five mixer-settler reactors (2.8 L) were placed in series (Fig. 1). The first reactor was filled with 1.25 L of cobalt–nickel feed, while all the other mixers were filled with 1.25 L of water. The ionic liquid was pumped (P_2) into the first reactor (MS_1) at a flow rate of 15 mL min^{-1}, while the phases were mixed. As soon as the reactor was filled, the aqueous feed solution was separately pumped (P_1) into the first mixer settler reactor at a flow rate of 14 mL min^{-1}. The start-up principle was maintained in a similar way for all other mixer-settlers. In the second reactor (MS_2), the pregnant ionic liquid was washed by pumping water (P_4) through it at a flow rate of 5.6 mL min^{-1}. In the following three mixer settlers (MS_{3-5}) the cobalt was stripped in counter current with water at a flow rate of 11.5 mL min^{-1} (P_3). All reactors were stirred at 700 rpm and the temperatures in the reactors were kept constant at 50 °C, using a heat-conducting ribbon. After 16 hours of circulation, the water phase was analysed for the cobalt, nickel, chloride and TOC content. The ionic liquid phase was analysed for the cobalt and nickel content.

Results and discussion

Trihexyl(tetradecyl)phosphonium chloride, commercially known as Cyphos® IL 101, was selected as the extraction phase, both acting as a solvent and an extractant for the selective extraction of cobalt from nickel in chloride media, because of its specific properties: hydrophobic character, a melting point below room temperature, commercial availability, and the absence of fluorinated anions.[21] This makes Cyphos® IL 101 an easily manageable, relatively cheap and environmentally friendly ionic liquid, which is suitable for use on an industrial scale. In an aqueous phase with high chloride concentrations, cobalt(II) will be present as an anionic tetrachlorocobaltate(II) complex (blue), whereas nickel(II) will be present as the hexaaquo complex (green). The anionic tetrachlorocobaltate(II) complex is extracted to the ionic liquid phase, while the hydrated nickel(II) ion stays in the aqueous phase making it possible to separate cobalt from nickel with Cyphos® IL 101. The back extraction (or stripping) of cobalt from the ionic liquid is possible with water; water lowers the electrolyte concentration forcing cobalt to reform a hexaaquo complex (pink).

The high viscosity of Cyphos® IL 101 (about 2500 cP at 20 °C)[21] made the implementation in a continuous extraction process challenging. Both presaturating the ionic liquid with water and heating up the ionic liquid up to 60 °C reduced its viscosity (to about 100 cP)[17] and made it manageable to transfer the highly viscous liquid through pumping. The experimental setup and all selected extraction parameters were carefully chosen on the basis of our previous work on the cobalt–nickel separation in a batch process.[17] The actual setup is shown in Fig. 1 and the schematic representation of the

Fig. 1 Operational continuous extraction process for the separation of cobalt from nickel with the trihexyl(tetradecyl)phosphonium chloride ionic liquid (Cyphos® IL 101) as the extraction phase. The different stages are (from left to right): an extraction stage, a washing stage and three stripping stages in counter-current mode.

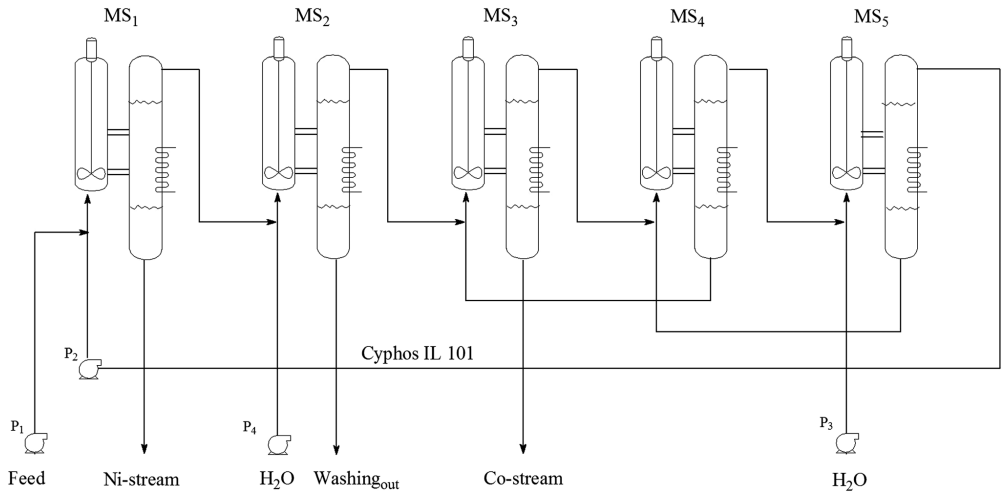

Fig. 2 Schematic representation of the continuous ionic liquid extraction process using the ionic liquid trihexyl(tetradecyl)phosphonium chloride, Cyphos® IL 101 (MS = mixer-settler; P = pump).

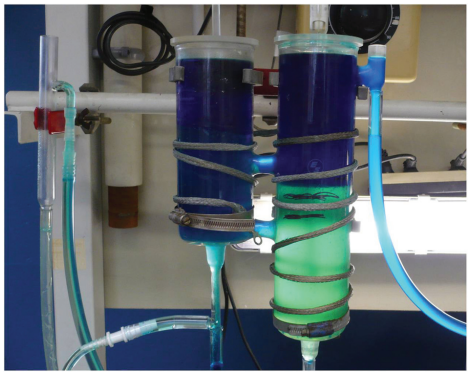

Fig. 3 Close-up of the first mixer-settler (MS_1, not operational) in which the cobalt extraction takes place: mixing compartment (left) and phase-settling compartment (right).

continuous extraction process is shown in Fig. 2. The cobalt extraction takes places in the first reactor (MS_1), leaving nickel in the aqueous raffinate. A close-up of the first reactor is shown in Fig. 3. The ionic liquid loaded with cobalt is then washed in the second reactor (MS_2) and in the last three stages (MS_3 to MS_5) cobalt is stripped from the ionic liquid solutions using water in the counter-current mode, forming the cobalt raffinate. The regenerated ionic liquid is directly fed back to MS_1 to extract a new load of cobalt.

After 16 hours of continuous cycling, the cobalt and nickel concentrations of the different aqueous streams were analysed (Table 1). It can be seen that the nickel raffinate contained only 21 ppm of cobalt, giving rise to a nickel purity of >99.5%. The removal of the residual cobalt impurities is discussed further in the text. After the washing stage, which was introduced to reduce the chloride content of the ionic liquid phase, the wash water contained small amounts of cobalt and nickel. These losses could be prevented by recycling the wash water back to the extraction circuit. The cobalt raffinate with a low nickel impurity level had a cobalt purity of >99.8%. Nearly all cobalt was removed from the ionic liquid phase after passing through three stripping stages.

A remark about the chloride contents before and after MS_1 has to be made: the aqueous feed had a chloride content of 7.6 M, whereas the chloride concentration in the nickel raffinate was only 6.4 M. This is because the ionic liquid that is used as the input in MS_1 originated from the after-stripping stage at MS_5. Due to the different stripping stages, the ionic liquid at this point was saturated with water. The chloride ions in the aqueous feed redistributed into the ionic liquid and decreased the chloride concentration of the aqueous phase by 14%. Since the distribution ratio of cobalt depends on the chloride concentration, this dilution effect also decreases the extraction efficiency of cobalt.[17] Further optimisation of the process is possible by using a pre-treatment step to increase the chloride concentration of the ionic liquid outlet stream of MS_5. Pretreatment of the outlet stream with the nickel raffinate, which has a 6.4 M chloride concentration, has two beneficial effects: (1) it will increase the chloride concentration of the ionic liquid stream; (2) removal of the cobalt impurities present in the nickel raffinate will lead to a more purified nickel solution. This pretreatment is equivalent to two mixer-settlers in counter-current mode.

Table 1 Cobalt, nickel, chloride and phosphonium cation concentrations in the different aqueous streams and in the ionic liquid outlet stream

	Co (mg L^{-1})	Ni (mg L^{-1})	Cl^- (M)	$[P_{66614}]^+$ (mg L^{-1})
Feed	5000	5000	7.6	—[a]
Ni raffinate (MS_1)	21	4900	6.4	43
Wash water (MS_2)	250	100	2.8	42
Co raffinate (MS_3)	5000	7	0.8	77
IL outlet (MS_5)	55	*n.d.*[a]	—	—

[a] — = not measured; *n.d.* = not detected.

Reagent losses from the extraction phase to the aqueous phase are inherent to solvent extraction processes. Typical losses during an extraction process for tertiary amines in acidic media are between 10 and 40 ppm.[22] In our extraction process, the loss of the phosphonium cation to the different aqueous streams was ranging from 40 to 80 ppm. These losses are thus comparable to the current state-of-the-art. However to further reduce the loss of ionic liquid cation in the aqueous phase, a salting-out process could be used,[23] and the ionic liquid could be recovered by nanofiltration.[24,25]

The separation of cobalt and nickel by solvent extraction from chloride media is on an industrial scale applied by Xstrata Nikkelverk, (Kristiansand, Norway), Sumitomo Metal Mining (Niihama, Japan) and Eramet (Le-Havre-Sandouville, France).[26] The Xstrata Nickelverk plant uses tri-isooctylamine as an extractant diluted in 17% of aromatic diluents.[27] The process makes use of four mixer-settlers in a counter-current mode to extract cobalt from the leach solution, several small mixer-settlers for the removal of nickel impurities and two mixer settlers for stripping of cobalt. The leach solution used as feed contains 220 g L^{-1} nickel and 11 g L^{-1} cobalt. After extraction, a nickel-rich solution of 60 g L^{-1} Ni and 0.03 g L^{-1} Co, and a cobalt-rich solution of 0.01 g L^{-1} Ni and 50 g L^{-1} Co are obtained. The ionic liquid continuous extraction process presented in this communication could be further developed to a process on an industrial scale and it presents certainly a cleaner technology than the currently used industrial processes. The green credentials of a continuous ionic liquid extraction process are mainly the non-volatility and non-flammability of the ionic liquid, since the emission of odorous volatile components (diluents, modifier and extractant) are avoided. This leads to environmentally friendlier and healthier working conditions. The features of the Xstrata process can be compared with that of our continuous ionic liquid process. Although the nickel concentration is much higher in the leach solution of the Xstrata process than in our experiments, a nickel-rich feed will not have a huge influence on the results, because nickel is barely extracted. However, the extraction efficiency is affected by the cobalt concentration due to change in the viscosity of the ionic liquid phase upon extraction of cobalt. Only relatively low cobalt loadings (<20 g L^{-1}) can be used. The viscosity of the ionic liquid phase will range between 100 and 150 cP after extraction, if the initial cobalt concentration in aqueous feed is similar to that of the Xstrata process (11 g L^{-1}).[17] However, the raffinate solutions of the Xstrata process are much more purified (about ten times higher) compared to our continuous ionic liquids process. Hence, our process still needs further optimization. This optimization includes introducing extra washing steps, which allows further removal of the nickel impurities from the organic phase. As suggested earlier, the use of a second mixer settler in the counter-current mode for cobalt extraction will further reduce the cobalt content in the nickel raffinate.

Conclusions

The proof-of-principle of a continuous ionic liquid extraction process for the separation of metals has been given. Cobalt and nickel could be separated using the ionic liquid trihexyl (tetradecyl)phosphonium chloride (Cyphos® IL 101) as the extraction phase. The setup with one extraction step, a washing step and three counter-current stripping steps gave pure cobalt (>99.8%) and nickel (>99.5%) streams. After stripping, the ionic liquid phase was regenerated. We have shown that ionic liquids can be implemented in industrially applied solvent extraction processes with an equal or even smaller number of mixer settler stages than the state-of-the-art industrial processes. The problems associated with the inherently higher viscosity of ionic liquid phases have been solved. Our process could be made competitive with the current industrially applied processes after applying minor optimizations. The continuous ionic liquid extraction process offers a more sustainable approach to solvent extraction by eliminating volatile and odorous compounds. This leads to environmentally friendlier and healthier working conditions.

Acknowledgements

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CHAPTER

4

ACID-SATURATED IONIC LIQUIDS: METAL OXIDE DISSOLUTION AND BACK-EXTRACTION

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Abstract

The dissolution of metal oxides in an acid-saturated ionic liquid, followed by selective stripping of the dissolved metal ions to an aqueous phase is proposed as a new ionometallurgical approach for the processing of metals in ionic liquids. The hydrophobic ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with a concentrated aqueous hydrochloric acid solution was used to dissolve CaO, NiO, MnO, CoO, CuO, ZnO and Fe_2O_3. It was found that nickel(II) and calcium(II) could be separated from all other transition metals present in the ionic liquid phase by stripping at high chloride concentrations. By scrubbing the ionic liquid solutions phase with water, manganese(II) and cobalt(II) could be stripped together with a fraction of iron(III) and copper(II), leaving zinc(II) and the remainder of copper(II) and iron(III) in the ionic liquids phase. These metal ions could be removed from the ionic liquid using ammonia. Copper(II) and zinc(II) formed ammine complexes and were back-extracted, while iron(III) precipitated as iron(III) hydroxide. After removal of all the metals present in the ionic liquid phase, the ionic liquid was prepared for reuse. Unfortunately, the mutual separations nickel-calcium, cobalt-manganese, or zinc-copper could not be achieved with this ionic liquid system. This system is useful when nickel is the metal of interest, since separation of nickel from all other transition metals present in the solution is achieved by one stripping step.

Introduction

Ionic liquids (ILs) are a relatively new class of solvents which are entirely made of ions and possess a melting point below 100 °C.[1] Other characteristic properties include a high electrical conductivity, a large electrochemical window, a broad liquidus range, and a high thermal stability.[2] These properties make ionic liquids perfectly suitable solvents for a broad range of applications fields, such as catalytic and chemical reactions,[3,4] membrane technology ,[5–7] separation technology,[7] nanotechnology ,[8–10] and analytical chemistry.[11,12] Solvent extraction (SX) is a technique often used to separate metal ions from each other,[13] and there have been a small number of reports of the utilisation of ionic liquids.[14–18] Trihexyl(tetradecyl)phosphonium chloride, the ionic liquid used in this study has been shown to be an environmentally friendly extraction phase for metal ions when applied in undiluted form.[19,20] In addition, ionic liquids can be used as solvents for the electrochemical recovery of metals[21,22]. For electrowinning, ionic liquids should have a high solubilizing power for metal salts, including metal oxides. However, the solubility of metal oxides in ionic liquids is in general very low, this is because no oxide-binding reagent able to react with the metal oxide is present and because of the high strength of many metal-oxide bonds. Nevertheless, some examples of ionic liquids that were able to dissolve

metal oxides have been reported.[22,23] Dai et al. and later Bell et al. reported the solubility of uranium(VI) oxide and vanadium(V) oxide, respectively, in imidazolium chlororoaluminate ionic liquids.[24,25] Unfortunately, chloroaluminate ionic liquids are not suitable for ionometallurgical processing of metal oxides, since these ionic liquids are extremely sensitive to moisture. Abbott and co-workers were able to dissolve a range of metal oxides in deep-eutectic solvents (DES), which are mixtures of choline chloride with a hydrogen-bond donor and are solvents with properties similar to those of ionic liquids.[26–29] Nockemann et al. used protonated betaine bis(trifluoromethylsulfonyl)imide and similar ionic liquids for the dissolution of several metal oxides including the rare-earth oxides, uranium(VI) oxide, zinc(II) oxide, copper(II) oxide and nickel(II) oxide .[30,31] These examples of ionic liquids were able to react with the oxides because of the presence of reactive protons in the cationic core of the ionic liquid. The availability of reactive protons is essential for the dissolution of metal oxides in ionic liquids. However, conventional protic ionic liquids cannot be used for this dissolution process, because upon reaction with the metal oxide, the ionic liquid is transformed into a neutral amine base. Moreover, many protic ionic liquids contain substantial amounts of neutral molecules, unless they are derived from very strong Brønsted acids.[32] Ionic liquids with acid anions such as hydrogen sulphate have been used for the leaching of metals from ores. Unfortunately, the number of possible anions is limited to partially deprotonated polyprotic acids.[33–36] Furthermore, hydrogen sulphate ionic liquid were used for the dissolution of alumina for electrolysis applications.[23,37]

In this paper we propose another approach to the dissolution of metal oxides in ionic liquids, namely by using an acid-saturated ionic liquid solution. More in particular, the dissolution of CaO, NiO, MnO, CoO, CuO, ZnO and Fe_2O_3 in the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with hydrochloric acid has been investigated. The stripping of the dissolved metals from the ionic liquid phase to an aqueous phase is described and the selective removal of metals from the ionic liquid offers possibilities for the separation of mixtures of metal ions especially for nickel. Finally, the regeneration of the ionic liquid is considered.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium chloride $P_{66614}Cl$ (>97%; Cyphos® IL 101; Cytec Industries), HCl (37 wt%, VWR), 1,4-dioxane (>99%; extra pure; stabilised, Acros Organics), ammonia (25 wt%, Chem-Lab NV), Fe_2O_3 (purified, Sigma-Aldrich), CaO (pieces made from marble, RPR), MnO (powder; 60 mesh; 99%, Sigma-Aldrich),

NiO (76% Ni, Acros Organics), CoO (95%; powder, Alfa Aesar), CuO (>99%, Sigma-Aldrich) and ZnO (>99%, Sigma-Aldrich) were used as received, i.e. without further purification.

Instrumentation and methods

The metal content of the ionic liquid phases and aqueous phases was determined using a bench top total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). For analysis of the aqueous phase by TXRF, aqueous samples (1 mL) were measured after addition of gallium as an internal standard. The samples were diluted with MilliQ water (if necessary). A small aliquot of 10 μL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 200 s. For the determination of the metal content in an organic phase by TXRF, a certain weight of the extracted phase (± 0.5 g) was diluted in dioxane (20 mL). Gallium (1000 mg L^{-1}, in HNO_3 2-3 %) was added to the solution as an internal standard. A small aliquot of 5 μL was applied on a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with a measurement time of 400 s. Absorption spectra were measured with a Varian Cary 5000 spectrophotometer. A quartz cuvette with an optical path length of 0.1 mm was used. ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 161.98 MHz for ^{31}P. The samples were measured in a NMR tube containing a sealed capillary with deuterated chloroform (an external lock). A delay time (d1) of 60 s was applied in the NMR pulse sequence to avoid saturation effects in the ^{31}P NMR.

Dissolution experiments

10 wt% hydrochloric acid (12 M HCl) was dissolved in the ionic liquid trihexyl(tetradecyl)phosphonium chloride (50 mL). To this solution, NiO, CuO, Fe_2O_3, ZnO, CaO, MnO and CoO were added with a metal concentration of 1 g L^{-1} for each metal. The ionic liquid solutions were analysed for their metal content after intensively stirring for two hours at 60 °C.

Stripping experiments

To carry out the stripping experiments, a sample (4 mL) of the P_{66614}Cl–HCl phase containing the dissolved metal ions was taken and mixed with an aqueous solution (4 mL). This aqueous solution contained HCl concentrations ranging from 0 M (pure water) to 12 M. The solutions were stirred for 30 minutes at 60 °C. After phase separation, the phases were centrifuged (3000 rpm, 3 min) and both phases were analysed for their metal content. The recovery of the ionic liquid was tested after stripping of copper, zinc and iron. To three individual batches of the P_{66614}Cl –HCl solution (5 mL), Fe_2O_3 and CuO and ZnO were added, respectively, so that after dissolution the ionic liquid phase had a metal content of 5 g L−1.

After the dissolution of the metal oxides, the ionic liquid solution was washed twice with water (5 mL). Thereafter, the ionic liquid phase was mixed with an aqueous ammonia solution (5 wt% NH3, 5 mL). After centrifugation the ionic liquid phases were analysed for their metal content. After the stripping step at 6 M HCl, the ionic liquid phase (4 mL), was subsequently mixed three times with a pure water solution (4 mL). Finally, an ammonia solution (5 wt%) was used as stripping solution (4 mL). The stripping conditions were the same as described in the previous paragraph; after each stripping step the phases were separated and after centrifugation the metal content was analysed in both phases.

The results of all the stripping experiments are represented by the stripping percentage (%S), which describes the percentage of a particular metal that is back-extracted from the ionic liquid phase to the aqueous phase. Depending on the metal concentration of the specific metal, either equation 4.1 or equation 4.2 was used to calculate the stripping percentage.

$$\%S = \frac{[M]_{aq}}{[M]_0} \tag{4.1}$$

$$\%S = \frac{[M]_0 - [M]_{IL}}{[M]_0} \tag{4.2}$$

Here $[M]_{aq}$ is the concentration of the metal in the aqueous phase after stripping, $[M]_{IL}$ is the concentration of the metal in the ionic liquid after stripping and $[M]_0$ is the initial concentration of the metal in the ionic liquid phase before stripping. Equation 4.1 was used when the metal element concentration was lower in the aqueous phase than in the ionic liquid phase after stripping. On the other hand, equation 4.2 was used when the ionic liquid phase contained the lowest metal element concentration. The lowest concentration was measured, because the absolute errors are much smaller and thus the %S value is more accurate.

Results and discussion

Dissolution experiments

For the dissolution of metal oxides in an acid-saturated ionic liquid several preconditions need to be fulfilled. First of all, the ionic liquid has to be able to dissolve a sufficiently large amount of acid to convert the required amount of metal oxides. Secondly, the ionic liquid must form two phases in contact with water to carry out the stripping experiments with an aqueous phase. Thirdly, a low solubility of the ionic liquid in water is required to minimise losses of the organic cations

to the aqueous phase in order to make the system viable from both an economic and environmental point of view.[22] Fourthly, the ionic liquid needs to be able to keep the metals dissolved, which can be achieved by using an ionic liquid with coordinating anions. Finally, in order to avoid a complicated extraction system it is favourable to choose the anion of the ionic liquid identical with the conjugated base of the acid. All these requirements are fulfilled by choosing the ionic liquid trihexyl(tetradecyl)phosphonium chloride saturated with a concentrated aqueous hydrochloric acid solution, P_{66614}Cl–HCl. Although the ionic liquid shows a very low solubility in water (10–80 ppm, depending on the electrolyte concentration), the ionic liquid is able to absorb up to 0.82 mole fraction of water, which corresponds to 13.5 wt% at room temperature.[20,38,39] The fact that water is soluble in the ionic liquid allows saturating the ionic liquid with concentrated hydrochloric acid (37 wt% HCl). Although dry trihexyl(tetradecyl)phosphonium chloride has a very high viscosity (1200 cP at 30 °C)[40] saturation of the ionic liquid with water and an increase in temperature cause a large decrease of the viscosity (about 100 cP at 60 °C) and allows an easier handling of the ionic liquid.[20] The solubility experiments were carried out by adding the metal oxides NiO, CuO, Fe_2O_3, ZnO, CaO, MnO and CoO with a metal concentration of 1 g L^{-1} for each metal to the trihexyl(tetradecyl)phosphonium chloride – hydrochloric acid mixture under intensive stirring for 2 h at 60 °C. The metal concentrations after dissolution of NiO, CaO, CoO, MnO, CuO, ZnO and Fe_2O_3 in P_{66614}Cl–HCl solution are reported in Table 4.1.

Table 4.1: Measured metal content of the P_{66614}Cl-HCl solution after dissolution of the oxides.[a]

Metal oxide	**Metal content (mg L^{-1})**
NiO	996(±2)
CaO	698(±36)
CoO	993(±10)
MnO	994(±27)
CuO	1035(±8)
ZnO	1041(±10)
Fe_2O_3	647(±11)

[a] To the acid-saturated ionic liquid, an amount of metal oxide was added, which would result after complete dissolution to a concentration of 1000 mg L^{-1}.

All added metal oxides, except Fe(III) and Ca(II), are quantitatively dissolved in the ionic liquid phase. Iron(III) oxide was not completely dissolved after two hours, and longer stirring times were needed for complete dissolution, which occurred after a period of a week. The low calcium content in the ionic liquid phase can be explained by the fact that the mixture becomes biphasic and finely dispersed aqueous droplets are formed upon dissolution of the metal oxides. These droplets settle at the bottom

of the flask and were therefore not included in the analysis. When the dispersed water droplets were analysed, the remaining part of the calcium content was found therein. Except calcium, no other metals were detected in the water droplets. This can be explained because all other metals are present as anionic complexes (vide infra), forming ion pairs with the phosphonium cations and staying dissolved in the ionic liquid phase. On the other hand, calcium is not able to form anionic complexes and is present as a hydrated calcium ion, which is easily transferred to the aqueous phase when the mixture starts to become biphasic. The biphasic behaviour can be explained by two effects by which the solution exceeds the saturation limit; firstly the dissolution of metal oxides is producing water as a reaction product and secondly the metal ions present in the solution can induce changes in the physical properties, such as water miscibility. Although relatively low metal concentrations were chosen to prove the dissolution of metal oxides in the acidified ionic liquid, the theoretical amount of metal oxides able to dissolve is determined by the amount of hydrochloric acid present in the ionic liquid solution and corresponds - in the system described in this paper - to 0.62 M for divalent metal oxides (e.g. for nickel this will be 36 g L^{-1}). However, divalent anionic chlorometallate complexes strongly influence the viscosity of the ionic liquid solution and practically the maximum metal loading is about 15–20 g L^{-1}.[20] The dissolution of metal oxides in acid saturated ionic liquids offers particular opportunities to bring metal ions in ionic liquid solution, which cannot enter the ionic liquid phase via extraction, such as calcium and nickel. As such it offers opportunities to further process these metals in the ionic liquid phase.[20] Furthermore, the dissolution of metal oxides (and in general metals salts) in an ionic liquid is of interest for metal extraction from one ionic liquid to another ionic liquid or to another organic phase.[41] The selectivities can be different from those observed for aqueous systems, since the solvation abilities of the metal ion in ionic liquids can be different with respect to an aqueous solution.

Knowledge of the metal speciation in the ionic liquid solution is of importance for optimisation of the ionometallurgical process. Although the divalent ions Ni(II), Co(II), Cu(II), Mn(II) and Zn(II) and the trivalent Fe(III) occur as tetrachlorometallate complexes in chloride based ionic liquids,[42–47] the occurrence of these ions in an acid-saturated ionic liquid solution has to be verified. The absorption spectra of the ionic liquid solutions containing the individual metal ions were recorded after dissolution of their metal oxides (Figure 4.1). Ni(II), Cu(II), Fe(III), and Co(II) were found to be present as their anionic tetrachlorometallate complexes. In Table 4.2 the absorption maxima for the different tetrachloro complexes are assigned and the absorption maxima correspond with literature data. Since the speciation of manganese(II) and zinc(II) could not be determined by optical absorption spectroscopy and since similar behaviour as the other metal species has been described in the literature, their existence as tetrachlorometallate(II) complexes is assumed.[48–50] The presence of calcium as a partly hydrated metal ion can be assumed and could explain why calcium is immediately transferred to the aqueous

phase as soon as biphasic behaviour occurs. The dissolution process of the metal oxides in the P66614Cl–HCl system are summarised in the following three equations: equation 4.3 is applicable to the divalent metals where M = Ni(II), Co(II), Zn(II), Cu(II), Mn(II), whereas equation 4.4 holds for Fe(III) and equation 4.5 for Ca(II).

$$2P_{66614}Cl+MO+2HCl \rightarrow [P_{66614}]_2[MCl_4]+H_2O \tag{4.3}$$

$$2P_{66614}Cl+Fe_2O_3+6HCl \rightarrow 2[P_{66614}][MCl_4]+3H_2O \tag{4.4}$$

$$P_{66614}Cl+CaO+2HCl+xH_2O \rightarrow [P_{66614}]\cdot CaCl_2.(H_2O)_{x+2} \tag{4.5}$$

Additionally, the dissolution of metal oxides in the acid saturated ionic liquid was compared with the dissolution in pure HCl solution (12 M HCl) and with the dissolution in the water saturated ionic liquid. It was found that dissolution of the acid-saturated ionic liquid was similar to the dissolution of metal oxides in hydrochloric acid, although for the acid-saturated ionic liquid longer reaction times were necessary because of the higher viscosity and slower mass transfer. On the

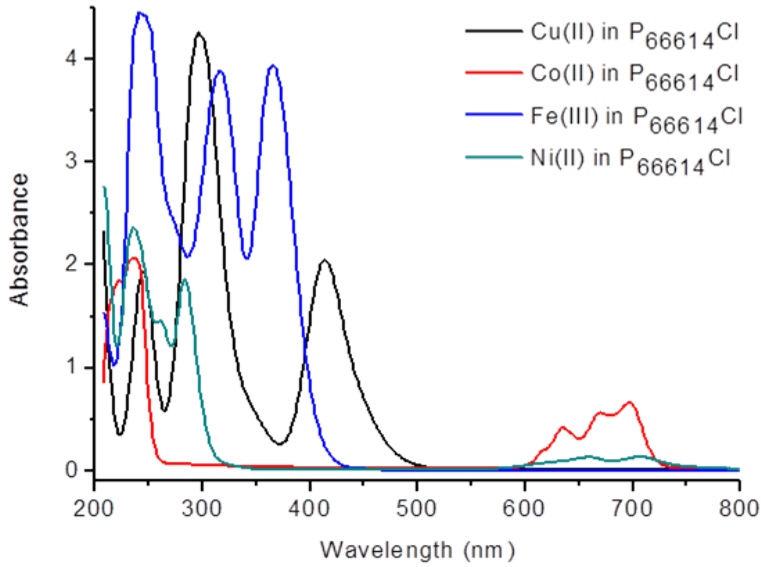

Figure 4.1: Absorption spectra of the individual tetrachlorometallate complexes after dissolution of their metal oxides in the $P_{66614}Cl$–HCl mixture (metal content is 5 g L^{-1}).

Table 4.2: Assignment of the absorption maxima typical for the tetrachlorometallate complexes present in the absorption spectra shown in Figure 1.

[MCl_4]$^{x-}$	λ_{max} **(nm)**	**Transition**	**References**
[$NiCl_4$]$^{2-}$	236, 261, 284	LMCT[a] ($Cl^- \rightarrow Ni^{2+}$)	51
	660, 708	$d-d$: $^3T_1(P) \leftarrow {}^3T_1$	52
[$CoCl_4$]$^{2-}$	236	LMCT ($Cl^- \rightarrow Co^{2+}$)	52,53
	697, 670, 636	$d-d$: $^4T_{1g}(P) \leftarrow {}^4A_2$	20,54
[$CuCl_4$]$^{2-}$	414, 296, 245	LMCT ($Cl^- \rightarrow Cu^{2+}$)	42,52,55
[$FeCl_4$]$^-$	243, 316, 247	LMCT ($Cl^- \rightarrow Fe^{3+}$)	52,56

[a] LMCT = ligand-to-metal transfer

contrary, the water saturated ionic liquid was not able to dissolve the metal oxides except for calcium oxide. As expected, the dissolution of the metal oxides in the acid-saturated ionic liquid can be fully ascribed to the reaction with the reactive protons of the added hydrochloric acid.

Stripping experiments

The stripping behaviour of the metal ions present in the trihexyl(tetradecyl)-phosphonium chloride – hydrochloric acid solution was investigated as a function of the hydrochloric acid concentration in the aqueous phase. One can argue about the term “stripping” (or back-extraction) instead of extraction since the metal ions were originally present in the ionic liquid solution and are extracted only once. Because stripping is generally used for the redistribution of a component from an organic phase to an aqueous phase, we will,therefore, use the term “stripping” for describing this experiment. Only aqueous hydrochloric acid solutions were considered because the conjugate base of this acid is the same as the anion of the ionic liquid and mixtures of anions would be undesirable. It was found that nickel and calcium are quantitatively back-extracted to the aqueous phase over the entire HCl concentration range (Figure 4.2). This can be explained by the strong tendency of nickel(II) and calcium(II) to form aqua complexes. Cobalt(II) and manganese(II) were partly back-extracted only at low HCl concentrations, but zinc(II) and copper(II) and iron(III) could not be removed from the ionic liquid phase. Based on the extraction behavior of the different metal ions, it is possible to separate calcium and nickel from manganese and cobalt and further from zinc, copper and iron. This system can be of special interest for the recovery of nickel from a mixture of metals, since nickel can be removed in one step from all other transition metals present in the solution. Nevertheless, the mutual separation of calcium from nickel, of cobalt from manganese, and of copper from zinc and iron with this ionic liquid system is impractical, because of the poor selectively of these separations.

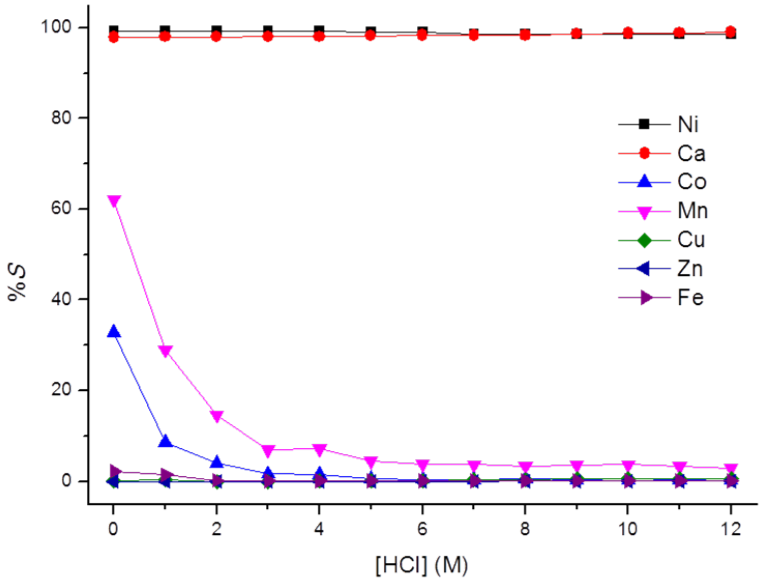

Figure 4.2: Stripping percentage (%S) of the different metal ions as a function of the HCl concentration in the aqueous phase.

Recovery the ionic liquid phase: removal of copper, zinc and iron

In order to reuse the ionic liquid, iron, copper and zinc have to be removed. For the removal of iron from trihexyl(tetradecyl)phosphonium chloride, stripping with EDTA was proposed.[19] Copper(II) and zinc(II) can be removed simultaneously with iron(III) by stripping with EDTA. However, since EDTA is too expensive for application in industrial hydrometallurgical processes, ammonia was tested as a stripping agent. In ammonia solutions, copper will form the complex $[Cu(NH_3)_4]^{2+}$ and zinc(II) the complex $[Zn(NH_3)_4]^{2+}$ which have a much higher stability constant ($\beta = 10^{12}$ and 10^9, respectively)[57,58] compared to the anionic chloro complexes $[CuCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ at low chloride concentrations ($\beta = 1$ and 10^1 respectively) and these complexes are easily transferred to the aqueous phase.[59–62] In these alkaline conditions iron will precipitate as iron(III) hydroxide. In a continuous process, the three phases (i.e. the recovered ionic liquid phase, the aqueous solution with copper(II) and zinc(II) and the iron(III) hydroxide precipitate) can be separated in one step by using a solid bowl centrifuge.[63] Figure 3 shows that after treatment the ionic liquid solution with an aqueous ammonia solution, copper(II) is stripped to the aqueous phase (right) and that iron(III) is precipitated, this precipitate is collected at the interface after centrifugation (left). After phase separation by centrifugation, no

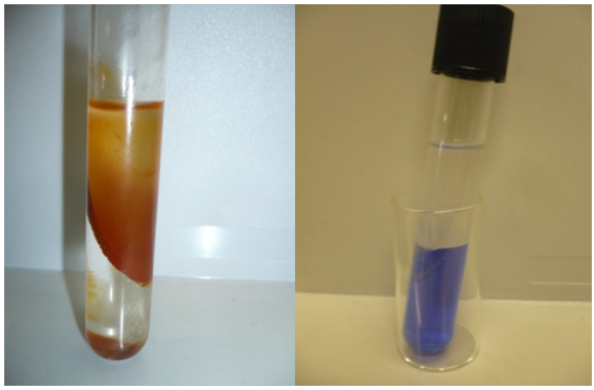

Figure 4.3: Left: iron hydroxide precipitate, formed upon treatment of the ionic liquid phase with an aqueous ammonia solution. Right: stripping of copper from the ionic liquid phase by an aqueous ammonia solution.

measurable metal content was found in the ionic liquid phase. In order to generate the ionic liquid phase for reuse, a pretreatment step consisting of washing the ionic liquid with an aqueous hydrochloric acid solution must be included.

Stability in the presence of ammonia

Although it was reported that tetraalkylphosphonium halides can be combined with concentrated sodium hydroxide without any degradation,[64–66] examples are reported where tetraalkylphosphonium salts dissolved in organic solvents are not always stable in the presence of hydroxides or other bases, forming a tertiary alkylphosphine oxide and an alkane.[64,67] Therefore, the stability of trihexyl(tetradecyl)phosphonium chloride was investigated after mixing the ionic liquid phase with an aqueous ammonia solution. ^{31}P NMR spectra of the ionic liquid phase were therefore recorded. The resonance signal of phosphine oxide situated at 49.6 ppm was integrated and compared to the resonance signal of trihexyl(tetradecyl)phosphonium cation at 32.7 ppm. The peak integration ratios were then compared with the ^{31}P NMR spectrum of trihexyl(tetradecyl)phosphonium chloride as it was received. It was found that the commercial trihexyl(tetradecyl)phosphonium chloride, already contained a small phosphine oxide content but no increase for the integration ratio was found on treatment with ammonia. This washing step is therefore justified as a process step, since no additional degradation of the ionic liquid was observed.

Multistep stripping

In order to remove the metals from the ionic liquid, a multistep stripping procedure was applied on the ionic liquid-acid solution. The first stripping stage made use of a 6 M HCl aqueous solution. Thereafter, the ionic liquid solution was washed three times with water. Finally, the ammonia stripping procedure just described was performed to recycle the ionic liquid for reuse. It was found that after the first acid extraction step extraction step, nickel and calcium were stripped with an efficiency of 99.1% and 98.3%, respectively (Table 4.3). However, impurities of manganese and cobalt were co-extracted to the aqueous phase (3.8% and 0.5%, respectively). After two washing stages with water, manganese (99%), cobalt (92.2%) and iron (35%) were removed from the ionic liquid phase. The distribution for cobalt, manganese and iron is strongly dependent on the hydrochloric acid concentration.[19] In order to remove the remaining cobalt (7.7%) and manganese (1%) from the ionic liquid phase, a third washing step was necessary. However, copper (14.6%) started to transfer to the aqueous phase at this stage. These facts highlight the difficult mutual separation of all transition metals except for nickel. Given the fact that nickel is separated from all other transition elements, this system is especially interesting for applications in which nickel needs to be removed from other transition metal impurities such as iron, cobalt, manganese, cobalt or zinc. Finally, iron, copper and zinc are removed from the ionic liquid phase applying stripping with ammonia. This leads to a metal-free ionic liquid that can be used for a new dissolution step of metal oxides. The schematic representation of the dissolution and subsequent stripping of the metal ions in the acid-saturated ionic liquid is shown in Figure 4.4.

Table 4.3: Cumulative stripping percentage (%S) after each stripping step.

step	stripping agent	Ni(%)	Ca(%)	Co(%)	Mn(%)	Cu(%)	Zn(%)	Fe(%)
1	6 M HCl	99.1	98.3	0.5	3.8	0.1	0.0	0.1
2	water	100	100	27.6	61.7	0.0	0.0	4.4
3	water	0.0	0.0	92.3	99	0.0	0.0	35
4	water	0.0	0.0	100	100	14.2	0.0	66.6
5	NH_3 (5 wt%)	0.0	0.0	0.0	0.0	100	100	100

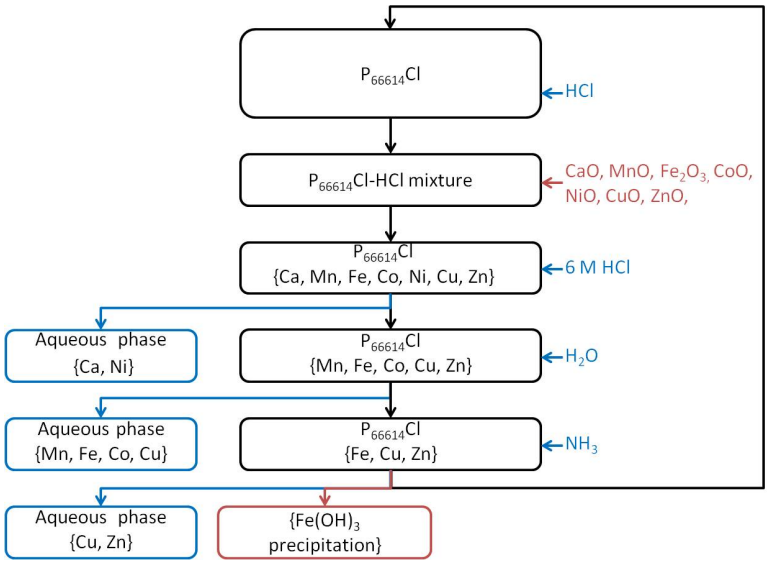

Figure 4.4: Flow chart for the dissolution of metal oxides and the separation of the dissolved metals by stripping to the aqueous phase: the ionic liquid stream is shown in black, the aqueous streams in blue and the metal oxides or metal hydroxides are shown in red.

Conclusions

The use of an acid-saturated ionic liquid system has been used to overcome the problem of low metal solubility in ionic liquids and allows further processing of the metal ions from the ionic liquid phase. Trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) saturated with hydrochloric acid was found to dissolve large amounts of the metal oxides, to be insoluble in the aqueous phase and to be stable to mildly basic aqueous ammonia solutions. The stripping of the dissolved metals from the ionic liquid to the aqueous phase was demonstrated; nickel and calcium were separated from cobalt, manganese, and copper, zinc and iron. The mutual separation between cobalt, manganese, copper and iron is difficult. Recovery of the ionic liquid was possible by changing the stripping conditions and the ionic liquid could be reused after removal of iron, zinc and copper by washing with an ammonia solution. This process is of particular interest for the separation of nickel from other transition metal ions, because nickel can be removed in one step from cobalt, manganese, iron, copper and zinc.

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CHAPTER

5

METAL EXTRACTION BETWEEN TWO MUTUALLY IMMISCIBLE IONIC LIQUIDS

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Supplementary information available in appendix A : ^{1}H NMR, UV-Vis absorption and ^{31}P NMR spectra.

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Separation of cobalt and nickel by solvent extraction with two mutually immiscible ionic liquids†

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The proof-of-principle for the separation of metals by solvent extraction using two mutually immiscible ionic liquids is given. Cobalt was extracted from the ionic liquid 1-ethyl-3-methylimidazolium chloride to the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate. A distribution ratio of 44 was obtained. Cobalt could be selectively separated from nickel, with a separation factor of 207. The extraction mechanism was elucidated using UV-VIS absorption measurements. The mutual solubility between the two ionic liquids was determined by ^{1}H NMR. Processing steps such as washing, stripping and regeneration of the ionic liquid phases are discussed.

Introduction

Solvent extraction (SX) is one of the most important hydrometallurgical processes in the refining of metals, especially of precious metals, rare earths and cobalt–nickel, by separation and purification.[1] Solvent extraction is based on the preferential distribution of the dissolved metal ions between two mutually immiscible phases, in general an aqueous phase and an organic phase. Transfer of the metal ion from one phase to the other is enabled by an extracting agent (extractant). During the last decade, considerable research efforts have been devoted to the replacement of the organic phase in solvent extraction systems by an ionic liquid.[2–9] Ionic liquids are solvents entirely consisting of ions.[10–12] They have a negligible vapour pressure, so they are non-volatile and have a very high flash point. Substitution of the volatile hydrocarbon-based organics by ionic liquids could lead to inherently safer and environmentally friendlier extraction processes. So far, most studies on the application of ionic liquids in solvent extraction processes have made use of ionic liquids with fluorinated anions, *e.g.* hexafluorophosphate or bis(trifluoromethylsulfonyl)-imide anions, because these ionic liquids are highly hydrophobic and hence immiscible with water. Unfortunately, fluorine-containing ionic liquids are expensive and there are issues with their stability (*e.g.* hydrolysis of hexafluorophosphate ions) and persistence in nature. There are a few examples of solvent extraction studies with non-fluorinated ionic liquids, and most of them make use of an organic solvent as diluent.[13–16] Recently, we developed a very efficient solvent extraction process for the separation of cobalt and nickel from chloride solutions based on the undiluted ionic liquid trihexyl(tetradecyl)phosphonium chloride as the organic phase.[17]

In this paper, we give the proof-of-principle for the separation of metal ions by distribution between two mutually immiscible ionic liquids. The example of separation of cobalt and nickel is discussed. Substitution of the aqueous phase by an ionic liquid phase in a solvent extraction process has several advantages. First of all, the extraction mechanism can be different, offering the possibility of changing the distribution ratios and improving the separation factors. Secondly, the more polar ionic liquid can be used as a leaching solution to dissolve metal oxides and metal salts.[18,19] This allows leaching at elevated temperatures, without the need for using autoclaves. More selective leaching is possible as well.[20,21] Mutually immiscible ionic liquids have been reported,[22–24] but their use in separation processes has been restricted to the extraction of organic compounds.[25] There exist some examples of extraction systems containing an inorganic molten salt and an organic phase,[26–28] but none for the metal distribution between two mutually immiscible ionic liquids.

Experimental

Chemicals

Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate (Cyphos® IL 104, >97%) and 1-ethyl-3-methylimidazolium chloride (>98%) were purchased from IoLiTec (Heilbronn, Germany).

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$CoCl_2$ (>97%), $NiCl_2$ (>98%), sulfuric acid (95–97%) were purchased from Sigma Aldrich. Dioxane (stabilized, 99.5%) was purchased from Acros Organics (Geel, Belgium). Ammonia (Analar Normapur, min 25 wt%) was purchased from VWR. All chemicals were used as received, without further purification.

Instrumentation and analysis methods

A Mettler Toledo DL 39 Karl Fischer Coulometer was used for determination of the water content in ionic liquids. To quantify the metal content, a benchtop total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker) was used. For quantification of the metal in $[P_{66614}][R_2POO]$ and $[C_2mim]Cl$, about 0.2 g of the ionic liquid solution was diluted in dioxane and water (20 mL), respectively. Then a gallium solution (in HNO_3) was added as an internal standard to the solution. An aliquot of 10 μL of solution was put on a quartz glass carrier, dried in a hot-air-oven at 60 °C, and then measured with a measurement time of 400 s. A Heraeus Megafuge 1.0 centrifuge was used for centrifugation of the samples after extraction. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for ^{1}H. The samples were dissolved in deuterated chloroform and the chemical shifts are given in ppm relative to tetramethylsilane (TMS). ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer, operating at 161.98 MHz for ^{31}P. The samples were dissolved in methanol-d_6. A delay time ($d1$) of 60 s was applied in the NMR pulse sequence to avoid saturation effects in the ^{31}P NMR spectra so that quantitative interpretation of the NMR spectra was possible. UV-VIS absorption spectra were recorded with a Varian Cary 5000 spectrophotometer, with a cuvette holder, which was heated to 80 °C by a circulating water bath. Quartz cuvettes with an optical path length of 0.1 mm were used to record the spectra of the highly absorbing solutions.

Extraction experiments

Cobalt extraction between two mutually immiscible ionic liquids

Cobalt(II) chloride (5 g L^{-1} Co) was dissolved in 1-ethyl-3-methylimidazolium chloride, $[C_2mim]Cl$, (5.55 g, 5 mL) at 95 °C and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate ($[P_{66614}][R_2POO]$ with R = 2,4,4-trimethylpentyl) (5 mL) was used as the extraction phase. The mixture of the two ionic liquids was stirred for 10 minutes at 95 °C and the metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Extraction between two mutually immiscible ionic liquids from a solution containing both cobalt and nickel

$CoCl_2$ and $NiCl_2$ (both with a metal concentration of 5 g L^{-1}) were dissolved in $[C_2mim]Cl$ (5.55 g, 5 mL) at 95 °C and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, $[P_{66614}][R_2POO]$ (5 mL) was used as extraction phase. The extraction was stirred for 10 minutes at 95 °C and the metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Washing of the extraction phase

The cobalt-loaded extraction phase (5 mL) was washed with water (5 mL) and stirred at 50 °C for 10 minutes. After washing, the phases were centrifuged (3000 rpm, 10 min) and the water phase was analyzed for its metal content.

Stripping of cobalt from the extraction phase

After extraction, cobalt was stripped from the $[P_{66614}][R_2POO]$ phase with a 2 M aqueous sulfuric acid solution. A volume ratio of 1 : 1 was used and the phases were stirred for 5 minutes at 50 °C. The metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Recovery of the extraction phase

The extraction phase $[P_{66614}][R_2POO]$ was regenerated after stripping by washing with an ammonia solution (2 M). A volume ratio of 1 : 1 was used and the phases were stirred for 5 minutes at 50 °C. The metal content in both phases was analyzed after centrifugation (3000 rpm, 5 min).

Distribution coefficients and separation factors

The distribution ratios for cobalt, D_{Co}, were calculated for all experiments, as follows:

$$D_{Co} = \frac{[Co]_{phos}}{[Co]_{im}} = \frac{[Co]_0 - [Co]_{im}}{[Co]_{im}} \quad (1)$$

where $[Co]_0$ is the initial cobalt concentration in the $[C_2mim]Cl$ phase before extraction, $[Co]_{im}$ is the cobalt concentration in the $[C_2mim]Cl$ phase after the extraction, and $[Co]_{phos}$ is the cobalt concentration in $[P_{66614}][R_2POO]$ after extraction. Distribution ratios for nickel, D_{Ni}, were calculated using the following equation:

$$D_{Ni} = \frac{[Ni]_{phos}}{[Ni]_{im}} = \frac{[Ni]_{phos}}{[Ni]_0 - [Ni]_{phos}} \quad (2)$$

where $[Ni]_0$ is the initial cobalt concentration in the $[C_2mim]Cl$ phase before extraction, $[Ni]_{phos}$ is the nickel concentration in the $[P_{66614}][R_2POO]$ ionic liquid after extraction, and $[Ni]_{im}$ is the nickel concentration in $[C_2mim]Cl$ after extraction. The efficiency of separation of cobalt from nickel is described by the separation factor:

$$\alpha_{Ni}^{Co} = \frac{D_{Co}}{D_{Ni}} \quad (3)$$

Results and discussion

Selection of a suitable pair of ionic liquids

Earlier work has shown that mixtures of some hydrophilic and some specific hydrophobic ionic liquids gave rise to two phases, in particular when there are large structural differences in either the cation or the anion.[22] Mutual immiscibility of the two ionic liquids is a necessary, but not sufficient condition. The hydrophilic ionic liquid, replacing the aqueous phase, needs to be an ionic liquid with coordination anions to enable

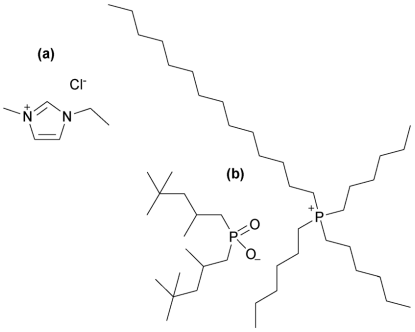

Fig. 1 Chemical structures of (a) 1-ethyl-3-methylimidazolium chloride, [C_2mim]Cl, and (b) trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, [P_{66614}][R_2POO].

the dissolution of inorganic metal salts. The hydrophobic ionic liquid, acting as the organic phase, has to be able to dissolve the extracted metal complex. In principle, an ionic liquid with a dissolved extractant could be used, but we preferred to look for a non-fluorinated ionic liquid with coordinating anions. Moreover, although the expression "mutually immiscible ionic liquids" is used, it must be realized that there is always a partial miscibility between any pair of ionic liquids. After screening of several ionic liquid combinations, the most promising system proved to be the one consisting of 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) and trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate, [P_{66614}][R_2POO] or Cyphos® IL 104 (Fig. 1). [P_{66614}][R_2POO] has been explored by other authors as extractant for metals.[29–31] Because the melting point of the ionic liquid [C_2mim]Cl is 77–79 °C, the extraction studies needed to be performed at elevated temperatures.

Metal extraction

The results for the extraction experiments are shown in Table 1. To be sure that the equilibrium condition was reached, the distribution ratio of an extraction with a stirring time of 10 minutes was compared with the distribution ratio of an extraction with a stirring time of 2 hours. For both stirring times, the distribution ratios for cobalt were identical, meaning that the extraction equilibrium was reached within 10 minutes. Therefore, a stirring time of 10 minutes was used for all further extraction experiments. A distribution ratio of 44.0 (±0.4) was found for the distribution of cobalt between the two mutually immiscible ionic liquids, for a solution with only $CoCl_2$ present. Under the same condition, nickel is hardly extracted to the [P_{66614}][R_2POO] phase (D_{Ni} = 0.06 (±0.008)). The extraction experiments showed a selectivity of cobalt. A separation factor between cobalt and nickel of 207 was obtained. In Fig. 2, the layering of the two mutually immiscible ionic liquids [C_2mim]Cl and [P_{66614}][R_2POO] on top of each other and the distribution of $CoCl_2$ and $NiCl_2$ between them is shown.

Comparing the separation factors calculated for the extraction experiment in which cobalt and nickel are present in two different solutions with the one in which both cobalt and nickel are present in the same solution (Table 1) shows that the separation factor is about 3.5 times lower in the latter case. This decrease in the separation factor is ascribed to the decrease in cobalt extraction, caused by a competition effect between cobalt and nickel to bind to the phosphinate ligands (*vide infra*).

To elucidate the extraction mechanism, the absorption spectra of cobalt(II) chloride dissolved in the [C_2mim]Cl ionic phase were compared with that of the extracted cobalt(II) complex in the ionic liquid [P_{66614}][R_2POO] (Fig. 3). The absorption spectrum of $CoCl_2$ in [C_2mim]Cl shows the typical spectrum of the tetrachlorocobaltate(II) complex, $[CoCl_4]^{2-}$.[32,33] The absorption spectrum of cobalt in [P_{66614}][R_2POO] is totally different, which excludes the extraction of cobalt(II) as an anionic tetra(chloro)cobaltate species. The absorption spectrum is similar to those reported in the literature for $Co(R_2POO)_2$,[31,34] indicating that cobalt(II) is present in [P_{66614}][R_2POO] as the tetrahedral $Co(R_2POO)_2$ complex. The following extraction mechanism is proposed:

$$[C_2mim]_2[CoCl_4] + 2[P_{66614}][R_2POO] \rightarrow 2[C_2mim]Cl + 2[P_{66614}]Cl + Co(R_2POO)_2 \quad (4)$$

Table 1 Summary of the analysis results for the distribution of cobalt and nickel between the ionic liquids [C_2mim]Cl and [P_{66614}][R_2POO] at 95 °C, calculated for cobalt and nickel present in two different solutions (column A), and for cobalt and nickel present in the same solution (column B)

Extraction parameters[a]	A	B
$[Co]_{im}$ (ppm)	110 (±1)	318 (±14)
$[Ni]_{phos}$ (ppm)	283 (±35)	332 (±4)
D_{Co}	44.0 (±0.4)	14.7 (±0.7)
D_{Ni}	0.060 (±0.008)	0.071 (±0.001)
SF_{Co-Ni}	733 (±104)	207 (±12)

[a] $[Co]_{im}$: cobalt concentration in [C_2mim]Cl after extraction; $[Ni]_{phos}$: nickel concentration in [P_{66614}][R_2POO] after extraction; D_{Co}: distribution ratio for cobalt; D_{Ni}: distribution ratio for nickel; SF_{Co-Ni}: separation factor for the cobalt–nickel separation.

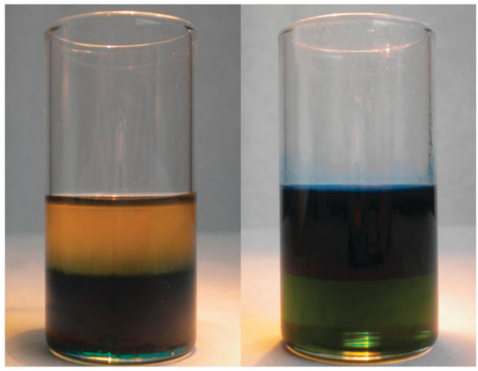

Fig. 2 Sample showing the ionic liquid [P_{66614}][R_2POO] layered on top of the ionic liquid [C_2mim]Cl, before (left) and after (right) cobalt(II) extraction.

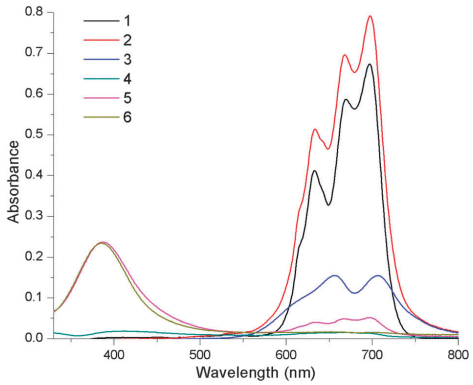

Fig. 3 Absorption spectrum of $CoCl_2$ and $NiCl_2$ dissolved in the ionic liquid $[C_2mim]Cl$ at 80 °C (optical path length of 0.1 mm), showing the presence of the $[CoCl_4]^{2-}$ and the $[NiCl_4]^{2-}$ anions and further of the octahedral nickel species $[NiCl_xR_2POO_y]^{2-x-y}$ after extraction. With spectrum 1 corresponding to $CoCl_2$ in $[C_2mim]Cl$ before extraction; 2 to $CoCl_2$ and $NiCl_2$ in $[C_2mim]Cl$ before extraction; 3 to $NiCl_2$ in $[C_2mim]Cl$ before extraction; 4 to cobalt in $[C_2mim]Cl$ after extraction; 5 to cobalt and nickel in $[C_2mim]Cl$ after extraction; and 6 to nickel in $[C_2mim]Cl$ after extraction.

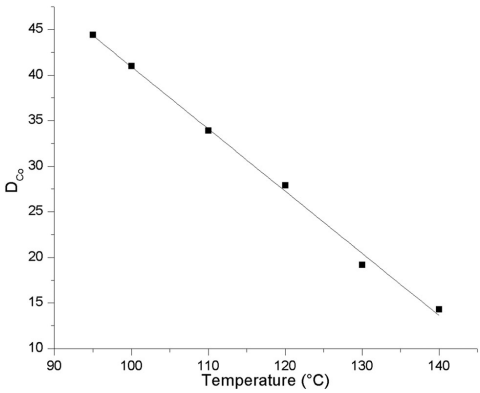

Fig. 4 Distribution ratio for cobalt(II) as a function of temperature.

In $[C_2mim]Cl$, cobalt(II) is present as the $[CoCl_4]^{2-}$ species. Upon mixing with $[P_{66614}][R_2POO]$, chloride ligands are replaced by phosphinate ligands, which have a high affinity for cobalt(II), and the $[Co(R_2POO)_2]$ species is formed. Due to the large structural similarity of this complex with the hydrophobic ionic liquid $[P_{66614}][R_2POO]$ it will prefer this phase, resulting in an extraction of cobalt from the $[C_2mim]Cl$ phase to the $[P_{66614}][R_2POO]$ phase. The absorption spectrum of $NiCl_2$ dissolved in $[C_2mim]Cl$ indicates that the $[NiCl_4]^{2-}$ species is present (Fig. 3).[32,33] After mixing of the nickel-containing $[C_2mim]Cl$ with $[P_{66614}][R_2POO]$, the color of the $[C_2mim]Cl$ phase switched from blue to pale yellow. The corresponding absorption spectrum with an absorption maximum at 381 nm is typical one that is expected for an octahedral nickel complex. It is assumed that octahedral mixed chloro-phosphinate nickel(II) complexes of the type $[NiCl_x(R_2POO)_y]^{(2-x-y)}$ are formed. These cannot be extracted due to their polar character. The formation of the mixed complexes implicates the loss of phosphinate ligands to the $[C_2mim]Cl$ phase.

Influence of temperature on the distribution coefficient

When the distribution ratio of cobalt was determined as a function of temperature between 95 and 140 °C, a linear decrease of the distribution ratio with temperature was observed (Fig. 4).

This behaviour can be explained by an increased solubility of both the phosphinate anion and the cobalt(II) phosphinate complex in the ionic liquid $[C_2mim]Cl$ with temperature. The solubility of $[R_2POO]^-$ in $[C_2mim]Cl$ was quantified at 140 °C, by ^1H NMR measurement after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes (see ESI†).

An increase in the phosphinate concentration of about 2000 ± 120 ppm was observed, compared to the solubility at 95 °C, which was about 1000 ppm. Because both the phosphinate and cobalt concentrations are increasing with temperature in the $[C_2mim]Cl$ phase after extraction, there will certainly be a correlation between these observations. To verify the influence of phosphinate ligand on the cobalt extraction, absorption spectra were measured of the $[C_2mim]Cl$ phase after extraction, both at 95 °C and 140 °C (Fig. 5). A weak broad absorption band, with absorption maxima at 667 and 640 nm is observed. This band lies in between the absorption bands of $[CoCl_4]^{2-}$ (697, 670, 633 nm) and those of $Co(R_2POO)_2$ at (640, 590 and 563 nm) (see ESI†), suggesting that both species are present in solution at a certain ratio. The increase of light absorption at 140 °C compared to the spectra measured at 95 °C also suggests the concentration increase of the phosphinate anion directly bonded to cobalt in the $[C_2mim]Cl$ phase. This is direct

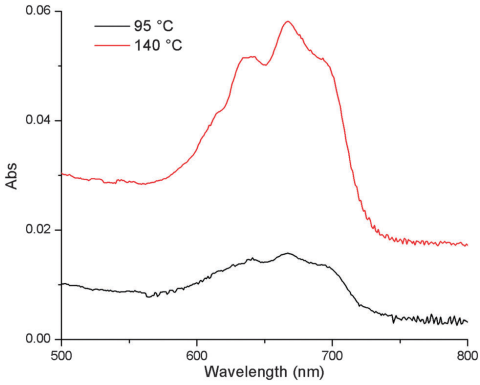

Fig. 5 Absorption spectra of the $[C_2mim]Cl$ phase after extraction at 95 and 140 °C.

evidence that the phosphinate concentration present in [C_2mim]Cl influences the cobalt extraction behavior. Upon extraction, the cobalt(II) phosphinate species are distributed over the two phases and this ratio is temperature dependent. This provides a logical explanation for the differences in distribution ratios at different temperatures.

Quantification of the mutual solubility

To quantify the solubility of [C_2mim]Cl in [P_{66614}][R_2POO], a ^{1}H NMR spectrum was recorded after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes at 95 °C. These conditions resemble those of the solvent extraction experiments (*vide supra*). The presence of [C_2mim]Cl in the [P_{66614}][R_2POO] phase was quantified by integrating characteristic resonances in the NMR spectrum, corresponding to one of the two ionic liquid molecules (see ESI†).[22,25,35] The peak at δ = 11.7 ppm, originating from the hydrogen atom at the C2 position of the imidazolium ring, was integrated and related to the integration of the peak at δ = 2.5 ppm, originating from the eight hydrogen atoms at the C1 position of the phosphonium cation. A solubility of 9.2 wt% (or 31 mol%) of [C_2mim]Cl in [P_{66614}][R_2POO] was determined from the ratio of the integrated peaks. The same procedure was applied to measure the solubility of the $[P_{66614}]^+$ cation in [C_2mim]Cl. The signals were too weak for a reliable integration. Although an accurate determination of the solubility of the phosphonium cation $[P_{66614}]^+$ in [C_2mim]Cl was not possible, it can be concluded that the solubility is very low. However, only measuring the solubility of the cation is not sufficient, since anions can exchange as well (phosphinate anions then replace chlorides). The solubility of the phosphinate anions can be measured by integration of the resonances in the ^{1}H NMR spectrum at δ = 0.89. A solubility of about 1000 ppm was found. Since the process is used for the extraction of cobalt, which has a high affinity for phosphinate ligands, the phosphinate concentration in [C_2mim]Cl is expected to be even lower, after mixing the phases.

Further processing steps

Because the solubility of [C_2mim]Cl in [P_{66614}][R_2POO] is about 9 wt% (*vide supra*), [C_2mim]Cl needs to be recovered from the extraction phase to avoid unacceptable losses of ionic liquid. [C_2mim]Cl dissolved in [P_{66614}][R_2POO] could be selectively removed from the cobalt-loaded [P_{66614}][R_2POO] phase by washing with a neutral water solution, because [C_2mim]Cl is water soluble and the other components, including the cobalt(II) phosphinate complex, are not, since this ionic liquid is immiscible with water. The [C_2mim]Cl content in the [P_{66614}][R_2POO] phase after the washing step was only 0.12 wt% (verified by ^{1}H NMR, see ESI†).

Only 7 ppm of cobalt was detected in the aqueous washing solution. [C_2mim]Cl could be recycled from the washing solution by evaporation of water. Cobalt was stripped from the [P_{66614}]-[R_2POO] ionic liquid phase by an aqueous 2 M sulfuric acid solution, by which the bonded cobalt ions will be exchanged by protons. In one single stripping step, the cobalt content in the [P_{66614}][R_2POO] extraction phase was reduced to 127 ppm,

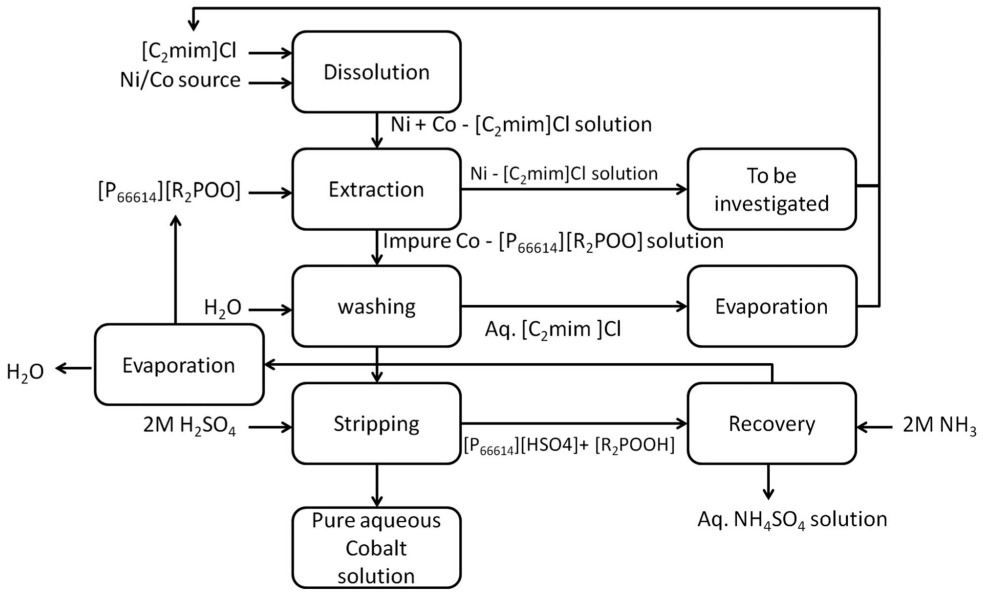

Fig. 6 Flow chart for cobalt–nickel separation using mutually immiscible ionic liquids.

showing that virtually all of the extracted cobalt could be recovered by stripping to the aqueous phase. Because phosphinic acid is formed during the stripping step (5), a deprotonation step is necessary to regenerate the phosphonium phosphinate ionic liquid (6):

$$[P_{66614}][R_2POO] + H_2SO_4 \rightarrow [P_{66614}][HSO_4] + R_2POOH \quad (5)$$

$$[P_{66614}][HSO_4] + R_2POOH + 2NH_3 \rightarrow [P_{66614}][R_2POO] + (NH_4)_2(SO_4) \quad (6)$$

This was achieved by washing the extraction phase which is immiscible with water, after stripping with a 2 M aqueous ammonia solution. After recovery, $[P_{66614}][R_2POO]$ contained 14.3 wt% of water, which had to be removed by evaporation before reuse of the ionic liquid in a next extraction experiment with two immiscible ionic liquids. To prove that a 1 : 1 phosphonium-to-phosphinate ratio was retained in the ionic liquid $[P_{66614}][R_2POO]$, the extraction, stripping and regeneration procedure was repeated in the absence of cobalt (to avoid paramagnetic impurities), and ^{31}P NMR spectra were recorded (see ESI†). A 1 : 1 ratio was found for the integration of the peaks at $\delta = 38.11$ and $\delta = 43.63$, corresponding to the trihexyl(tetradecyl)phosphonium cation and bis(2,4,4-trimethylpentyl)phosphinate anion, respectively. It can be concluded that no components of the ionic liquid $[P_{66614}][R_2POO]$ are lost during the processing procedure. All processing steps used for the cobalt–nickel separation are summarized in the flow chart shown in Fig. 6.

Conclusion

For the first time the separation of metals by solvent extraction using two mutually immiscible ionic liquids has been shown. Cobalt was extracted from the ionic liquid 1-ethyl-3-methylimidazolium chloride to the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate. A distribution ratio of 44 was obtained. Cobalt could be selectively separated from nickel, with a separation factor of 207. Stripping of cobalt from the hydrophobic phosphonium ionic liquid phase, followed by regeneration of the ionic liquid, was demonstrated, showing the potential of the method for use in a continuous extraction process. By replacement of the aqueous phase in solvent extraction by an ionic liquid phase, one can no longer speak about a hydrometallurgical process. The term to use is ''ionometallurgy''[36] or ''solvometallurgy'', rather than hydrometallurgy.

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CHAPTER

6

DISSOLUTION OF METAL OXIDES IN IMIDAZOLIUM IONIC LIQUIDS

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Carbene formation upon reactive dissolution of metal oxides in imidazolium ionic liquids†

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Metal oxides were found to dissolve in different imidazolium ionic liquids with a hydrogen atom in the C2 position of the imidazolium ring, but not if a methyl substituent was present in the C2 position. The crystal structure of the product that crystallised from an ionic liquid containing dissolved silver(I) oxide showed that this was a silver(I) carbene complex. The presence of carbenes in solution was proven by ^{13}C NMR spectroscopy and the reactions were also monitored by Raman spectroscopy. The dissolution of other metal oxides, namely copper(II) oxide, zinc(II) oxide and nickel(II) oxide, was also studied in imidazolium ionic liquids and it was found that stable zinc(II) carbenes were formed in solution, but these did not crystallise under the given experimental conditions. A crystalline nickel(II) carbene complex could be obtained from a solution of nickel(II) chloride dissolved in a mixture of 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium acetate.

Introduction

Since metal oxides are insoluble in most organic solvents, the processing of metal oxides is currently done in aqueous solutions.[1,2] Although water is generally considered as a green solvent, it must be realized that hydrometallurgical processing of metal oxide concentrates often requires large volumes of water and that large amounts of waste water are generated. Therefore, there is an interest in alternative solvents for the processing of metal oxides under ambient conditions. In the last decade a new class of solvents, namely ionic liquids (ILs), has been developed. Ionic liquids are solvents that consist entirely of ions. Many ionic liquids have a melting point below 100 °C and they have properties like a high thermal stability, a wide liquidus range, nonvolatility and nonflammability. These solvents have shown the ability to dissolve a large variety of organic and inorganic compounds, including metal oxides.[3–6] *Ionometallurgy* is the ionic liquid analogue of hydrometallurgy.[7] Dai *et al.* were able to dissolve UO_3 in imidazolium chloroaluminate ionic liquids.[8] Billard and coworkers found that UO_2, UO_3, Nd_2O_3, Eu_2O_3 and Pr_6O_{11} powders could be dissolved in the ionic liquid 1-methyl-3-butyl-imidazolium bis(trifluoromethylsulfonyl)imide after addition of small amounts of nitric acid.[9] Abbott and coworkers were able to dissolve a range of metal oxides in deep-eutectic solvents (DES), which are mixtures of choline chloride with a hydrogen-bond donor (*e.g.* urea, ethylene glycol, carboxylic acids) that show similar properties to ionic liquids.[10,11] The functionalized ionic liquid betainium bis(trifluoromethylsulfonyl)imide showed selective solubility towards a range of metal oxides.[12,13] The strongly bonded oxide anion is one of the problems associated with the digestion of the metal oxides in ionic liquids (or DES). The most straightforward method for digestion of a metal oxide in an ionic liquid is the addition of an acid which consumes the oxide anion with formation of water:

$$MO_y + 2yHX \rightarrow MX_{2y} + yH_2O \quad (1)$$

Functionalized ionic liquids that contain acidic protons are able to react with metal oxides and solvate the liberated metal ion in the solution.[13] Ionic liquids with imidazolium cations are one of the more common types of ionic liquids, but they do not contain protons that can be easily released.

We have tested the suitability of imidazolium ionic liquids for the dissolution of selected metal oxides. In some cases, we found that metal oxides were soluble in these imidazolium ionic liquids and that the dissolution mechanism proceeded *via* proton exchange at the C2 position of the imidazolium ring to form water and an N-heterocyclic carbene (NHC). In particular, we focused on the reaction with silver(I) oxide as it is already well known from studies on homogeneous catalysts that silver can form N-heterocyclic carbenes.[14–20] All literature reports on carbene formation make use of an organic solvent (*e.g.* dichloromethane, methanol) and not a pure ionic liquid.[15,21–23]

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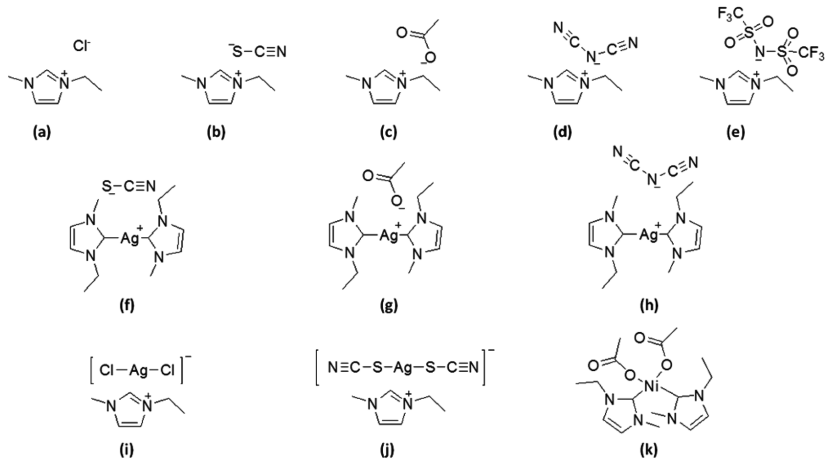


Fig. 1 Overview of the chemical structures of the discussed compounds: (**a**) 1-ethyl-3-methylimidazolium chloride, (**b**) 1-ethyl-3-methylimidazolium thiocyanate, (**c**) 1-ethyl-3-methylimidazolium acetate, (**d**) 1-ethyl-3-methylimidazolium dicyanamide, (**e**) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (**f**) bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I) thiocyanate, (**g**) bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I) acetate, (**h**) bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I) dicyanamide, (**i**) 1-ethyl-3-methylimidazolium dichloroargentate(I), (**j**) 1-ethyl-3-methylimidazolium dithiocyanatoargentate(I), and (**k**) bis(1-ethyl-3-methylimidazol-2-ylidene)nickel(II) acetate.

In this paper, the dissolution of silver(I) oxide in undiluted imidazolium ionic liquids with linear alkyl chains and with chloride, thiocyanate, acetate and dicyanamide anions is reported. Carbene formation has been found to be the driving force for the dissolution of silver(I) oxide. The reactivity of imidazolium ionic liquids was tested for dissolution of other metal oxides: copper(II) oxide, zinc(II) oxide and nickel(II) oxide. An overview of all chemical structures of the discussed ionic liquids, carbene complexes and other proposed compounds is presented in Fig. 1.

Experimental

Instrumentation and methods

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer, operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. The samples were dissolved in DMSO-d_6 and the chemical shifts are given in ppm relative to tetramethylsilane (TMS). Elemental analyses (carbon, hydrogen and nitrogen) were obtained using a CE Instruments EA-1110 elemental analyser. ESI mass spectra were recorded on a Thermo Finnigan LCQ Advantage mass spectrometer. DSC traces were recorded under a helium atmosphere using a Mettler-Toledo DSC822e module with a heating/cooling rate of 10 °C min^{-1}. Indium was used as a standard for temperature and enthalpy calibrations. The IR spectra were recorded in attenuated total reflectance mode on a Bruker Vertex 70 FTIR spectrometer at a resolution of 4 cm^{-1}. Raman spectra were recorded using a Bruker Vertex Ram II spectrometer using 150 mW laser power (Nd-YAG; 1064 nm) for 32 scans at a resolution of 4 cm^{-1}.

Crystals of complexes [Ag(C$_2$mim-ylide)$_2$][SCN], [Ag(C$_2$mim-ylide)$_2$][DCA], [Ag(C$_2$mim-ylide)$_2$][OAc] and Ni(C$_2$mim-ylide)$_2$-(OAc)$_2$ suitable for single crystal X-ray diffraction were glued on a nylon loop attached to a copper pin and placed at room temperature on an Agilent SuperNova diffractometer using Mo Kα radiation (λ = 0.71073 Å). The absorption corrections were applied using CrysAlisPro.[24] All structures were solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.[25] All hydrogen atoms were placed in calculated positions and refined using a riding model. In the structure of [Ag(C$_2$mim-ylide)$_2$][SCN], due to the space group symmetry the SCN anion is disordered over two positions. Also the H atoms on the methyl group of the cation were disordered and modelled over two positions rotated by 60° from each other. A summary of the crystallographic data can be found further in the Experimental section and Table 1 contains pertinent bond lengths, angles and geometrical values. CCDC-968222–968225 contain the supplementary crystallographic data for this paper. The program OLEX2 was also used in refinement and making pictures of the structures.[26]

Table 1 Bond lengths, angles, torsions and plane–plane angles from the crystal structures of [Ag(C$_2$mim-ylide)$_2$][DCA], [Ag(C$_2$mim-ylide)$_2$][SCN] and [Ag(C$_2$mim-ylide)$_2$][OAc]

	[DCA]	[SCN]	[OAc]
Ag–C/Å	2.075(3)	2.084(2)	2.108(2)
C–Ag–C/°	180.0(2)	179.56(11)	161.26(11)
C–N–C–C/°	91.2(5)	−83.0(3)	88.6(3)
Plane–plane/°	0.0(3)	55.09(7)	53.32(6)

The metal contents in the ionic liquids were determined using a bench top total reflection X-ray fluorescence (TXRF) spectrometer (Picofox S2, Bruker). A certain mass of the ionic liquid solution (approx. 0.1 g) was dissolved in an aqueous HCl solution (0.1 M, 20 mL). Gallium was added as an internal standard. A 5 μL aliquot of the test solution was applied onto a quartz glass carrier, dried by evaporation in a hot air oven (60 °C) and measured with an exposure time of 400 s.

Chemicals

1-Ethyl-3-methylimidazolium chloride (>98%), 1-ethyl-3-methylimidazolium thiocyanate (>98%), 1-ethyl-3-methylimidazolium dicyanamide (>98%), 1-ethyl-3-methylimidazolium acetate (>95%), 1-butyl-3-methylimidazolium acetate (>98%), 1-butyl-3-methylimidazolium chloride (>98%), 1-hexyl-3-methylimidazolium chloride (>98%), 1-octyl-3-methylimidazolium chloride (>98%), 1-decyl-3-methylimidazolium chloride (>98%), 1-butyl-2,3-dimethylimidazolium chloride (99%) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (>99.5%) were purchased from Iolitec (Heilbronn, Germany). Silver(I) oxide (>99%) was purchased from Alfa Aesar, and zinc(II) oxide (>99%), copper(II) oxide (>99%) and anhydrous nickel(II) chloride were purchased from Sigma-Aldrich. Nickel(II) oxide (76% Ni) was purchased from Acros Organics. All chemicals were used as received, without further purification.

Dissolution of silver(I) oxide in 1-alkyl-3-methylimidazolium ionic liquids. Silver(I) oxide (0.75 g, 15 w%) was added to [$C_x$mim][X] (4.25 g) (with x = 2, 4, 6, 8, 10 and X = chloride (Cl^-), thiocyanate (SCN^-), dicyanamide (DCA^-) and acetate (OAc^-)) at 90 °C, and the mixture was stirred until the reaction was completed (typically overnight).

Dissolution of silver(I) oxide in 1-butyl-2,3-dimethylimidazolium chloride and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Silver(I) oxide (0.1 g, 2 wt%) was added to [C_4dmim][Cl] or [C_2mim][NTf_2] (4.9 g) (at 90 °C) and the mixture was stirred overnight.

Dissolution of NiO, CuO and ZnO in 1-ethyl-3-methylimidazolium ionic liquids. 15 wt% of the metal oxide [= 176 mg (MO) g^{-1} (IL)] was added to 1-ethyl-3-methylimidazolium acetate or chloride and stirred at 90 °C overnight. The solution was filtered and the filtrate analyzed for its metal content.

General procedure for the formation of [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][X]. After dissolution of silver(I) oxide in the ionic liquid, the hot solution was filtered over a 0.45 μm glass micro fiber syringe filter (GMF) to remove undissolved Ag_2O and Ag particles. When cooling the filtrate to room temperature, crystals started to form and the solution was placed in a refrigerator overnight to complete crystallisation. The sample was centrifuged (3000 rpm, 10 min), the liquid was decanted and crystals were further purified by washing them with toluene. Finally the crystals were dried *in vacuo* at room temperature.

Analytical data for [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][thiocyanate] ([Ag(C_2mim-ylide)$_2$][SCN]). IR (ATR, $\tilde{\nu}$/cm^{-1}): 3143 ν(CH), 3099 ν(CH), 2975 ν(CH), 2948 ν(CH), 2872 ν(CH), 2056 ν(C≡N), 1632, 1564, 1468, 1448, 1438, 1410, 1379, 1352, 1265, 1219, 1167, 1105, 1092, 1034, 955, 924, 906, 845, 796, 769, 746 ν(CS), 727, 669, 646, 621, 606, 453, 411. NMR: δ_H (300 MHz, DMSO-d_6): 1.40 (t, 3H, C**H**$_3$–CH$_2$), 3.84 (s, 3H, N–CH$_3$), 4.18 (q, 2H, CH$_3$–C**H**$_2$–N), 7.49 (d, 2H, CH-*ar*); δ_c (75 MHz, DMSO-d_6): 17.13, 38.08, 45.92, 121.43, 122.99, 129.21, 180.25. ESI(+)MS calc. for $C_{12}H_{20}AgN_4^+$: m/z = 327.1, 329.1; found: m/z = 326.8, 328.8. CHN analysis: Calc. for $C_{13}H_{20}AgN_5S$ (386.26): C, 40.42; H, 5.22; N, 18.13%. Found: C, 40.83; H, 4.56; N, 18.02%. Melting point: 108 °C. **Crystal data** for $C_{13}H_{20}AgN_5S$ (M = 386.27): colourless block 0.30 × 0.08 × 0.03 mm^3, monoclinic, space group $C2/c$ (no. 15), a = 16.7075(11) Å, b = 8.1360(5) Å, c = 13.3162(8) Å, β = 111.810(7)°, V = 1680.53(18) Å^3, Z = 4, T = 298(2) K, μ(Mo Kα) = 1.321 mm^{-1}, D_{calc} = 1.527 g mm^{-3}, 10 704 reflections measured (5.66 ≤ 2Θ° ≤ 58.2), 2066 unique (R_{int} = 0.0229) which were used in all calculations. The final R_1 was 0.0266 (>2σ(I)) and wR_2 was 0.0600 (all data).

Analytical data for [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][dicyanamide] ([Ag(C_2mim-ylide)$_2$][DCA]). IR (ATR, $\tilde{\nu}$/cm^{-1}): 3149 ν(CH), 3111 ν(CH), 3089 ν(CH), 3010 ν(CH), 2979 ν(CH), 2951 ν(CH), 2227 ν(C≡N), 2191 ν(C≡N), 2127 ν(C≡N), 1743, 1639, 1566, 1470, 1452, 1441, 1410, 1385, 1358, 1311, 1261, 1221, 1169, 1109, 1090, 1032, 951, 898, 874, 798, 771, 727, 673, 648, 621, 513, 461, 405. NMR: δ_H (300 MHz, DMSO-d_6): 1.40 (t, 3H, C**H**$_3$–CH$_2$), 3.84 (s, 3H, N–CH$_3$), 4.17 (q, 2H, CH$_3$–C**H**$_2$–N), 7.49 (d, 2H, CH-*ar*); δ_c (75 MHz, DMSO-d_6): 17.13, 38.08, 45.93, 118.9, 121.5, 123, 178.4. ESI(+)MS calc. for $C_{12}H_{20}AgN_4^+$: m/z = 327.1, 329.1; found: m/z = 326.9 328.8. CHN analysis: Calc. for $C_{14}H_{20}AgN_7$ (394.22): C, 42.65; H, 5.11; N, 24.87%. Found: C, 42.62; H, 4.74; N, 25.10%. Melting point: 104 °C. **Crystal data** for $C_{14}H_{20}AgN_7$ (M = 394.24): colourless block 0.40 × 0.10 × 0.04 mm^3, monoclinic, space group $C2/c$ (no. 15), a = 20.344(2) Å, b = 6.9249(4) Å, c = 15.2990(17) Å, β = 126.766(16)°, V = 1726.6(3) Å^3, Z = 4, T = 298(2) K, μ(Mo Kα) = 1.175 mm^{-1}, D_{calc} = 1.517 g mm^{-3}, 3572 reflections measured (6.4 ≤ 2Θ° ≤ 58.58), 1981 unique (R_{int} = 0.0217) which were used in all calculations. The final R_1 was 0.0360 (>2σ(I)) and wR_2 was 0.0901 (all data).

Analytical data for [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][acetate] ([Ag(C_2mim-ylide)2][OAc]). IR (ATR, $\tilde{\nu}$/cm^{-1}): 3143 ν(CH), 3082 ν(CH), 2964 ν(CH), 2872 ν(CH), 1574 ν(C=O), 1562, 1470, 1450, 1377 ν(CO), 1319, 1261, 1223, 1176, 1126, 1107, 1092, 993, 955, 903, 866, 798, 760, 725, 663, 633, 613, 459, 407. NMR: δ_H (300 MHz, DMSO-d_6): 1.40 (t, 3H, C**H**$_3$–CH$_2$), 1.51 (s, 3H, CH$_3$–COO), 3.84 (s, 3H, N–CH$_3$), 4.18 (q, 2H, CH$_3$–C**H**$_2$–N), 7.50 (d, 2H, CH-*ar*); δ_c (75 MHz, DMSO-d_6): 17.10, 26.21, 38.08, 45.89, 121.44, 123.00, 172, 179. ESI(+) MS calc. for $C_{12}H_{20}AgN_4^+$: m/z = 327.1, 329.1; found: m/z = 326.9, 328.8. CHN analysis: Calc. for $C_{14}H_{23}AgN_4O_2$ (387.23): C, 43.42; H, 5.99; N, 14.47. Found: C, 42.69; H, 7.03; N, 13.52. Melting point: 94 °C. **Crystal data** for $C_{14}H_{23}AgN_4O_2$ (M = 387.23): colourless block 0.50 × 0.15 × 0.15 mm^3, monoclinic, space group $C2/c$ (no. 15), a = 15.4432(7) Å, b = 8.6443(4) Å, c = 13.5597(6) Å, β = 108.450(5)°, V = 1717.13(13) Å^3, Z = 4, T = 298(2) K, μ(Mo Kα) = 1.183 mm^{-1}, D_{calc} = 1.498 g mm^{-3}, 3891 reflections measured (5.86 ≤ 2Θ° ≤ 58.28), 1974 unique

(R_{int} = 0.0127) which were used in all calculations. The final R_1 was 0.0237 (>2$\sigma(I)$) and wR_2 was 0.0643 (all data).

Procedure for the formation of [bis(1-ethyl-3-methylimidazol-2-ylidene)nickel(II)][acetate]. After dissolution of anhydrous nickel(II) chloride (20 wt%) in 1-butyl-3-methylimdazolium acetate, an equal volume of 1-ethyl-3-methylimidazolium acetate layer was placed on top; by diffusion over time a few yellow crystals were formed. These crystals were harvested and used for the crystal structure determination, but it was impossible to characterise this compound in bulk. **Crystal data** for $C_{16}H_{26}N_4NiO_4$ (M = 397.12): yellow block 0.40 × 0.10 × 0.04 mm^3, monoclinic, space group $C2/c$ (no. 15), a = 12.4371(15) Å, b = 9.8200(10) Å, c = 15.9240(19) Å, β = 97.565(12)°, V = 1927.9(4) Å^3, Z = 4, T = 298(2) K, μ(Mo Kα) = 1.033 mm^{-1}, D_{calc} = 1.368 g mm^{-3}, 4251 reflections measured (5.7 ≤ 2Θ ≤ 57.44), 2205 unique (R_{int} = 0.0445) which were used in all calculations. The final R_1 was 0.0632 (>2$\sigma(I)$) and wR_2 was 0.1954 (all data).

Results and discussion

Reactivity of silver(I) oxide with 1-ethyl-3-methylimidazolium chloride

When 15 wt% silver(I) oxide was added to the ionic liquid 1-ethyl-3-methylimidazolium chloride, an instant vigorous reaction was observed and the oxide completely dissolved after about 2 hours at 90 °C. However, virtually no solubility of silver(I) oxide was found in other types of ionic liquids that were tested, such as quaternary ammonium ionic liquids. The dissolution reaction was monitored by ^{13}C NMR and the chemical shift of the carbon nucleus in the 2-position of the imidazolium ring shifted dramatically from about 136 ppm in the pure ionic liquid to about 179 ppm on the formation of a carbene (Fig. 2). Also the resonances of all the other carbon nuclei in the compounds were shifted by 2 to 3 ppm, so it can be clearly seen in the ^{13}C spectra that the solution consists of a mixture of the starting ionic liquid and its carbene form.

Silver(I) carbene complexes have previously been reported especially as N-heterocyclic carbene catalysts.[14–18,27,28] The carbene formation by reaction between 1-ethyl-3-methylimidazolium chloride and silver(I) oxide is known.[21,29] However, the reaction has always been carried out in a molecular solvent, such as methanol or dichloromethane. This paper reports for the first time on reactions of silver(I) oxide in undiluted ionic liquids, which both act as solvent and reagent. Furthermore the reactions for different alkyl chain lengths and ionic liquid anions have been investigated.

Silver carbenes complexes with halide anions are known to be relatively stable against moisture and light.[30] Reactions have even been carried out in water as a solvent.[31] The silver(I) carbene complexes in the chloride ionic liquids [C$_x$mim][Cl] were found to be stable to moisture and light. No degradation of the solution was observed over a period of several weeks.

Influence of alkyl chain length

The reaction between silver(I) oxide and other 1-alkyl-3-methylimidazolium chloride ionic liquids [C$_x$mim][Cl] (x = 4, 6, 8, 10) was also tested. Carbene formation could clearly be identified by ^{13}C NMR for all these ionic liquids, irrespective of the alkyl chain length. No crystals could directly be isolated from any of the ionic liquid solutions. In the literature, liquid-crystalline behaviour has been reported for silver(I) N-heterocyclic carbenes with imidazole moieties with longer alkyl chain lengths [Ag((C$_{16}$H$_{33}$)$_2$im-ylide)$_2$Cl] (im-ylide = imidazol-2-ylidene) when it was mixed with the corresponding imidazolium salt [(C$_{16}$H$_{33}$)$_2$im-ylide-H][Cl] in a 1 : 1 ratio.[15]

Reactivity of silver(I) oxide with methyl substituted imidazolium at the C$_2$ position

The solubility of silver(I) oxide in 1-butyl-3-methylimidazolium chloride [C$_4$mim][Cl] was compared with its solubility in 1-butyl-2,3-dimethylimidazolium chloride [C$_4$-2,3-dmim][Cl], in which the acidic hydrogen atom at the C2 position on the imidazolium ring is substituted by a methyl group. This substituent blocks the formation of an imidazolylidene carbene. However, an unexpected reaction of Ag_2O with imidazolium methyl substituted at the C2 position to form silver NHC complexes through oxidative cleavage of the C–C bond has been reported.[32] In the case of [C$_4$mim][Cl] a very good solubility of Ag_2O was found, whereas in the case of [C$_4$-2,3-dmim][Cl] no reaction between Ag_2O and the ionic liquid was observed. This confirms that carbene formation is proceeding by deprotonation of the carbon atom in the C2 position. Therefore, the presence of a hydrogen atom on the C2 carbon atom of the

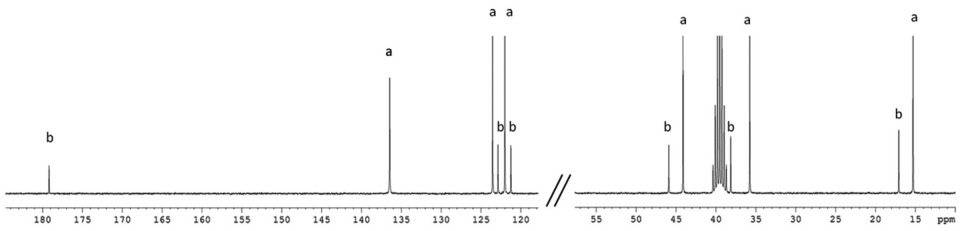


Fig. 2 ^{13}C NMR spectrum of [C$_2$mim][Cl] after reaction with 15 wt% of Ag_2O. Resonances from [C$_2$mim][Cl] are labeled with **a** and resonances from the ylide with **b**. The multiplet at 39.5 ppm is from the DMSO-d_6 solvent.

imidazolium ring is a requirement for dissolution of silver(I) oxide in imidazolium ionic liquids.

Reaction with imidazolium ionic liquids with other anions

1-Ethyl-3-methylimidazolium ionic liquids ([C_2mim][X], where X = thiocyanate (SCN^-), dicyanamide (DCA^-), acetate (OAc^-) or bis(trifluoromethylsulfonyl)imide (Tf_2N^-)) with different anions were tested as reactive solvents for dissolution of silver(I) oxide. Silver(I) oxide was found to dissolve in [C_2mim][SCN], [C_2mim][DCA] and [C_2mim][OAc], but not in [C_2mim][Tf_2N]. On cooling the reaction mixtures, single crystals suitable for structure determination by X-ray diffraction were obtained in [C_2mim][SCN], [C_2mim][DCA] and [C_2mim][OAc]. The crystal structure determinations showed that compounds of formulae [Ag(C_2mim-ylide)$_2$][SCN] (Fig. 3), [Ag(C_2mim-ylide)$_2$][DCA] (Fig. 4) and [Ag(C_2mim-ylide)$_2$][OAc] (Fig. 5) had been formed in the respective ionic liquids. All the crystal structures belong to the monoclinic space group *C*2/*c*, but with different unit cell parameters. A common feature is that the crystallographic asymmetric units contain one half of the cation and one half of the anion, with the remainder being generated by symmetry operations. The silver center has a linear or near linear two-coordinate silver(I) ion coordinated *via* the carbon in the 2-position of the imidazolium ring of two ylides, wherein the Ag–C bond lengths are in the expected ranges (Table 1).[33] In [Ag(C_2mim-ylide)$_2$][DCA] the two planes created by the imidazole units are coplanar, but those in the other compounds are twisted with respect to each other (Table 1). All three structures have the two ethyl groups of the coordinated C_2mim-ylide moieties on opposite sides in a *transoid* conformation. The ethyl groups do not lie in the plane of the imidazolium moiety as shown by the C2–N–C–C torsion angles (Table 1). In contrast to the chloride-containing carbene complexes, it was observed for the anions [SCN], [DCA] and [OAc] that the ionic liquid solutions containing the silver(I) carbene complexes degraded by forming a black precipitate after a period of several weeks exposed to air and light. However, this degradation was not observed during the first few days after synthesis. The isolated solid products [Ag(C_2mim-ylide)$_2$][X] did not show any degradation over the period of several weeks exposed to air and light.

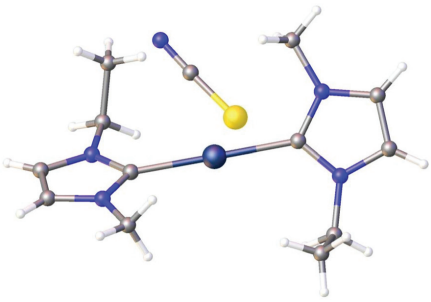


Fig. 3 View of the crystal structure of [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][thiocyanate]. The disorder of the SCN anion and H atoms on the CH_3 group is not shown.

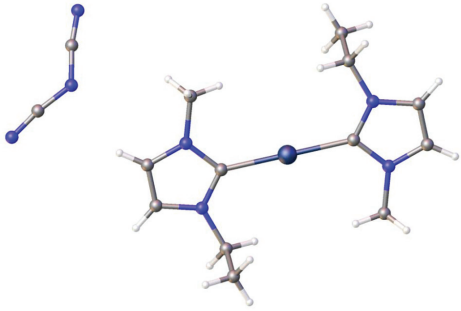


Fig. 4 View of the crystal structure of [bis-(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][dicyanamide].

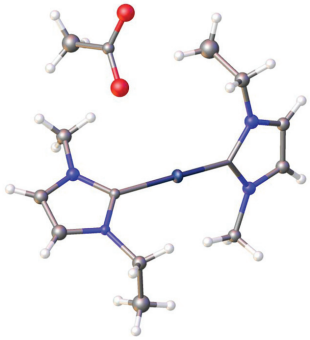


Fig. 5 View of the crystal structure of [bis(1-ethyl-3-methylimidazol-2-ylidene)silver(I)][acetate].

Mechanism of Ag-NHC formation

For stoichiometric reactions in molecular solvents between silver(I) oxide and imidazolium rings with short chains three main structures of silver carbenes have been reported:[16,17,19,20,34] namely, one where silver is linearly bonded to the halide and carbene (($C_xC_x$im)AgX), dimers with two bridging halides ($C_xC_x$im)-Ag-(μ^2X)$_2$-Ag-($C_xC_x$im) and a cationic bis(imidazolylidene)silver(I) balanced with dihalogenoargentate anion [Ag($C_xC_x$im-ylide)$_2$]$^+$[AgX_2]$^-$.

The reaction mechanism of the formation of silver NHC complexes from silver(I) oxide has previously been extensively investigated with density functional theory (DFT) computations by Hayes *et al.*[34] More in particular, they investigated the reaction mechanism between silver(I) oxide and two 1,3-dimethylimidazolium iodide moieties [C_1mim][I] in

dichloromethane with the formation of two (C_1mim-ylide)AgX compounds. In their reaction mechanism, the authors proposed that first an exergonic deprotonation step occurs which is driven by the strong basicity of the Ag_2O and this step is then followed by an exergonic metalation, with only a low energy barrier for which the transition state is stabilised by a second imidazolium cation. The products formed at this intermediate step are AgOH and (C_1mim-ylide)AgI, but with the 'AgOH' stabilised by interactions with the new ylide complex (eqn (2)). The next step is a second deprotonation in which silver(I) hydroxide abstracts the proton of a second imidazolium cation and a second metalation step now without an imidazolium assisting the reaction forming a second (C_1mim-ylide)-Ag-I complex (eqn (3)). The overall reaction is given by eqn (4).

$$Ag_2O + [C_1mim][I] \rightarrow AgOH + (C_1mim\text{-}ylide)AgI \quad (2)$$

$$AgOH + [C_1mim][I] \rightarrow H_2O + (C_1mim\text{-}ylide)AgI \quad (3)$$

$$Ag_2O + 2[C_1mim][I] \rightarrow 2[(C_1mim\text{-}ylide)AgI] + H_2O \quad (4)$$

To achieve the final product with two carbenes coordinated to the same Ag center ($[Ag(C_xC_xim\text{-}ylide)_2]^+$) a rearrangement reaction is required (reaction (5)).

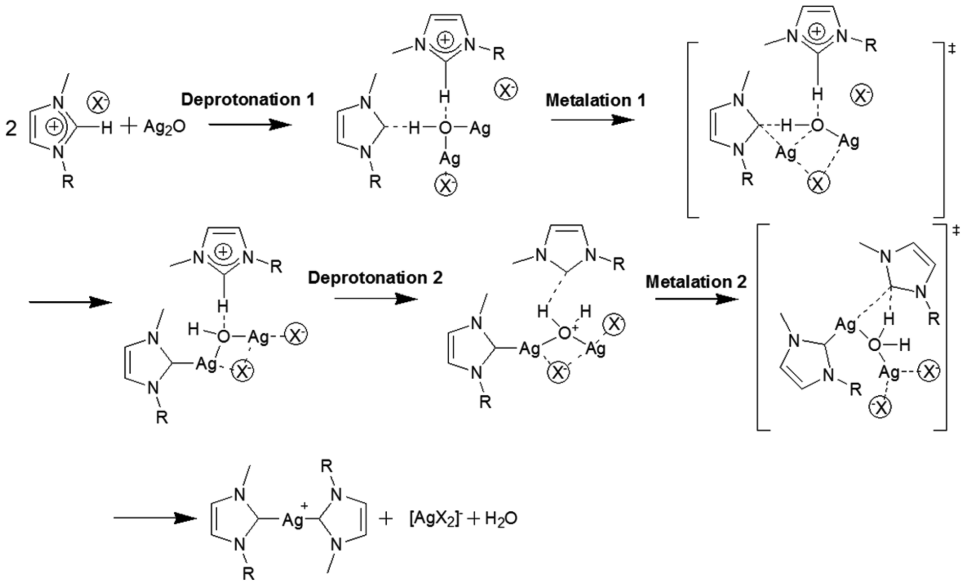
$$2[(C_xC_xim\text{-}ylide)AgX] \rightleftarrows [Ag(C_xC_xim\text{-}ylide)_2]^+[AgX_2]^- \quad (5)$$

This equilibrium is known to exist and has been extensively reviewed by Lin *et al.*[17] In ionic liquid solvents, the equilibrium is likely to lie on the right hand side due to the ionic nature of the solvent and products.

However, one has to be aware that reactions in ionic liquids can follow different pathways than in molecular solvents.[35–37] Whilst dichloromethane is a somewhat polar solvent, the ionic nature of the ionic liquid solvents may favour more ionic intermediates so species like [($C_xC_x$im-ylide)AgX] may not get formed at all. We propose that in the case of the [$C_x$mim][X] compounds studied here as pure ionic liquids, the process begins with the same barrier-less and exergonic deprotonation step, followed by a low barrier and exergonic metalation to form a complex of formation [($C_x$mim-ylide)AgXAgOH$\cdots$($C_x$mim)][X] (Scheme 1). This complex acts as the base and deprotonates the second imidazolium moiety and then metalation occurs by the silver center that is already coordinated by the carbene leading to a [Ag($C_x$mim-ylide)$_2$] cation, a $[Ag_2X]^-$ anion and a molecule of water (Scheme 1) rather than two molecules of [($C_xC_x$im-ylide)AgX] proposed by Hayes *et al.*[34] The highly ionic nature of the ionic liquid would favour the formation of two ionic species over the formation of two separate neutral [($C_x$mim-ylide)AgX] complexes.[35–37]

The solid products isolated in the cases of [Ag($C_x$mim-ylide)$_2$][X] ([X] = [SCN], [DCA] and [OAc]) are formed by anion exchange of the formed $[Ag(C_xmim\text{-}ylide)_2]^+[AgX_2]^-$ complex and the ionic liquid giving the following as the overall reaction scheme:

$$Ag_2O + 3[C_2mim][X] \rightarrow [Ag(C_2mim\text{-}ylide)_2][X]_{(s)} + H_2O + [C_2mim][Ag(X)_2]_{(dissolved)} \quad (6)$$



Scheme 1 Proposed mechanism for the reaction between Ag_2O and imidazolium ionic liquids of the type [$C_x$mim][X] (with X = Cl^-, SCN^-, DCA^- or OAc^-).

The formation of the $[AgX_2]^-$ anion was shown by speciation studies of the silver(I) complexes in $[C_x mim][SCN]$ investigated by *in situ* Raman spectroscopy. The shift in the $\nu_{C\equiv N}$ stretching vibration of the [SCN] anion is very indicative of the coordinating nature of the anion. The spectra of the homogeneous solutions, the neat ionic liquid and the crystal are shown in Fig. 6. The stretching vibration $\nu_{C\equiv N}$ of pure $[C_2mim][SCN]$ at 2055 cm^{-1} is partly shifted to 2080 cm^{-1} in the silver-containing $[C_2mim][SCN]$ solution, which indicates coordination of the thiocyanate anion to the Ag^+ ion. A linear $[Ag(SCN)_2]$ anion is the most probable product as the new peak corresponds with the $\nu_{C\equiv N}$ of the $[Ag(SCN)_2]^-$ complex observed in other non-aqueous solvents.[38] The Raman spectrum of the filtrate, after crystallisation of the $[Ag(C_2mim\text{-}ylide)_2][SCN]$, shows that the absorption band of the coordinated thiocyanate anions was intensified compared to that of the uncoordinated thiocyanate anion due to the depletion of thiocyanate anions from the solution by precipitation as the $[Ag(C_2mim\text{-}ylide)_2][SCN]$ complex and so a net increase of the $[Ag(SCN)_2]^-$ anion is observed.[39,40] The spectrum of the pure $[Ag(C_2mim\text{-}ylide)_2][SCN]$ shows a peak at 2061 cm^{-1} indicating the presence of non-coordinating thiocyanate groups. This peak is slightly shifted compared to pure $[C_2mim][SCN]$ due to the former being in the solid state and the latter in the liquid state.

The dissolution of silver(I) oxide in $[C_2mim][X]$ (X = SCN, DCA or OAc) also occurred at room temperature, but the reactions were slower, because the ionic liquids have a much higher viscosity compared to molecular solvents, especially at room temperature. At elevated temperatures the viscosity is lower and there is more energy to overcome the energy barriers of the reaction.

The fact that silver(I) oxide does not react with $[C_2mim][NTf_2]$ in the ionic liquid solution but does react when performed in a molecular solvent is puzzling.[23] Looking at the reaction mechanism, the first deprotonation step requires the transformation of solid Ag_2O into an intermediate Ag(OH)Ag species that is brought into solution and stabilised by a hydrogen-bond with the formed carbene, a free imidazolium moiety and Ag–anion interactions (Scheme 1). With $[NTf_2]^-$ having the least coordinating ability of the anions studied, it is reasonable to propose that the $[NTf_2]^-$ anion cannot stabilise the $[(C_x mim\text{-ylide})AgXAgOH\cdots(C_x mim)[X]]$ intermediate without the additional solvation effects of a molecular solvent.

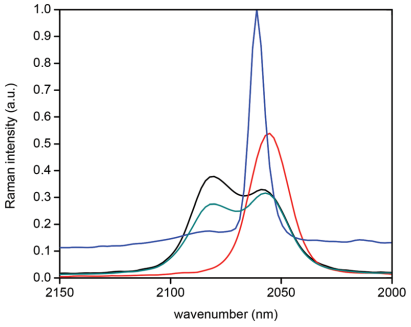


Fig. 6 Raman spectra between 2150 and 2000 cm^{-1} of $[C_2mim][SCN]$ (red), $[(C_2mim\text{-ylide})_2Ag][SCN]$ (blue), Ag(I)-containing-$[C_2mim][SCN]$-solution (green) and the filtrate (black).

Reactivity of ZnO, NiO and CuO in imidazolium ionic liquids

Other metal oxides were tested for their reactivity in imidazolium ionic liquids, in particular CuO, NiO and ZnO in $[C_2mim][X]$ (X = Cl, OAc). Table 2 reports the amount of the metal oxides that could be dissolved in the ionic liquid and shows that both CuO and ZnO show appreciable solubility in $[C_2mim][Cl]$, whereas only ZnO is well soluble in $[C_2mim][OAc]$. NiO is slightly soluble in $[C_2mim][Cl]$, but only poorly soluble in $[C_2mim][OAc]$.

In the case of ZnO, the dissolution product could be investigated by ^{13}C NMR spectroscopy since Zn^{2+} is a diamagnetic ion. The undissolved material was filtered off from the solution and the ^{13}C NMR spectra were recorded in DMSO-d_6. Carbene formation was observed in both the chloride and acetate imidazolium ionic liquids, as indicated by the large shift of the carbon nucleus in the C2 position of the imidazole ring (Fig. 7). However, in contrast to the spectra recorded from the silver(I) ylides, two peaks appeared in the carbene region. In $[C_2mim][OAc]$, these peaks were at 175.1 and 174.2 ppm with an approximate relative intensity ratio of 2 : 1 (Fig. 7 (bottom); the resonance of the COO^- group of the OAc anion at 173.9 ppm also appears in this region). The same intensity ratio was also found in $[C_2mim][Cl]$ with the resonances at 173.2 and 172.8 ppm (Fig. 7 (top)). Also, the chemical shifts of all the other carbon nuclei in the spectrum showed two new small peaks due to the ylide formation, shifted by 2 to 3 ppm relative to the parent imidazolium nuclei. The formation of two new peaks with a 2 : 1 ratio is also seen in the ^1H NMR spectrum. The fact that two new peaks appear (instead of one as for the silver complex) can possibly be ascribed to two different coordination environments around the Zn^{2+} ion. For instance, zinc(II) could be coordinated as $[Zn(C_2mim\text{-ylide})_2X_2]$ or as $[Zn(C_2mim\text{-ylide})X_3]^-$. Unfortunately no crystals could be isolated from the solution for further investigation of the structure of the carbene complexes.

Previous reports on zinc ylides with N-heterocyclic carbenes are rare as reported in a recent review article by Budagumpi *et al.*[41] One example is the 1-butyl-3-methylimidazolylidene zinc complex $[ZnBr_2(C_4mim\text{-ylidene})_2]$ which was directly synthesized from the corresponding ionic liquid $[C_4mim]Br$ using

Table 2 Dissolution of CuO, NiO and ZnO in $[C_2mim][Cl]$ and $[C_2mim][OAc]$ at 90 °C reported as mg (MO) g^{-1} (IL)

	$[C_2mim][Cl]$	$[C_2mim][OAc]$
CuO	64	2.3
NiO	5	0.9
ZnO	36	83

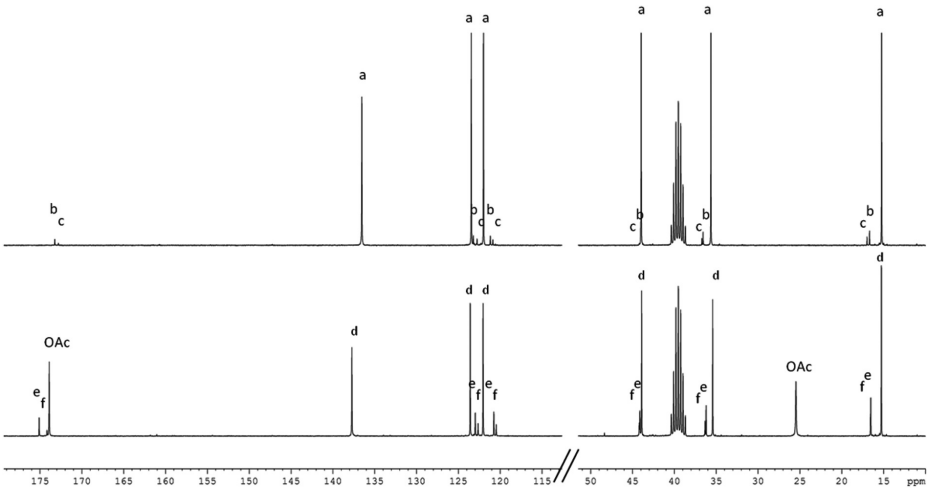


Fig. 7 ^{13}C NMR spectra showing carbene formation upon addition of ZnO to $[C_2mim][Cl]$ (top) (peaks from $[C_2mim][Cl]$ are indicated with label **a** and peaks from the ylide with labels **b** and **c**) and to $[C_2mim][OAc]$ (bottom) (peaks from $[C_2mim]^+$ indicated with label **d** and peaks from the ylide with labels **e** and **f**).

diethyl zinc ($ZnEt_2$).[42] In contrast to $ZnEt_2$ which must be handled in moisture-free environments, we show that zinc carbene complexes can be formed starting from ZnO and that zinc carbenes are relatively stable in non-dried ionic liquid solution.

The solutions formed by dissolution of copper(II) oxide and nickel(II) oxide in the imidazolium ionic liquids could not be investigated by ^{13}C NMR, because of their paramagnetic behaviour.

In a related study, but using $NiCl_2$ as a nickel source instead of NiO, crystals of a nickel carbene complex were isolated. 20 wt% of $NiCl_2$ could be dissolved in $[C_4mim][OAc]$. However in the case of $[C_2mim][OAc]$ when 15 wt% $NiCl_2$ was dissolved at 90 °C, a yellow amorphous solid was found to precipitate, although an appreciable amount of Ni^{2+} stayed dissolved in the solution (82 mg g^{-1}). Characterisation of the species formed in the solid and liquid states proved difficult so a crystallisation experiment was devised to slowly introduce $[C_2mim][OAc]$ by way of layering into the 20 wt% $NiCl_2$ solution in $[C_4mim][OAc]$. After several days, small yellow crystals appeared in the solution and these were characterised by single crystal X-ray diffraction and found to be a nickel(II) N-heterocyclic carbene complex of formula $[Ni(C_2mim\text{-}ylide)_2]$-$[OAc]_2$. Although several crystals were formed it was not possible to isolate a bulk sample so that no bulk analysis results are available.

Nickel(II) N-heterocyclic carbene compounds are relatively common, but most of these compounds have large substituents such as diisopropyl on the imidazolium rings, as seen, for example, in diiodo bis(1,3-diisopropylimidazol-2-ylidene)-nickel(II).[43] These authors also report N-heterocyclic carbenes with less bulky substituents such as diiodo bis(1-methyl-3-propylimidazol-2-ylidene)nickel(II).[43] There exist no literature reports about nickel(II) N-heterocyclic carbene compounds with acetate ligands,[33] although $Ni(OAc)_2$ is quite frequently used as a starting material in these syntheses.[43–45] The formation of carbenes in acetate ionic liquids has been studied by other research groups and the H atom at the C2 position of the imidazolium ring is known to be exchangeable and could protonate the acetate anion, so that the $[C_2mim]^+$ cation and the acetate anion are in equilibrium with the carbene and acetic acid.[35,46] In the case of $[Ni(C_2mim\text{-}ylide)_2][OAc]_2$, the carbene forms a complex with the Ni^{2+} ion and then precipitates from the solution.

The structure of the $[Ni(C_2mim\text{-}ylide)_2][OAc]_2$ crystals was collected in air at room temperature, showing their relative stability, and was found to be in monoclinic space group *C2/c* with the complex lying on a crystallographic two-fold axis. The nickel centers are square planar with the two ylides and the two acetate ligands *cis* to each other (Fig. 8).

This *cis* orientation of two ylides has only been seen before in bis(1,3-di-isopropylimidazol-2-ylidene)bis(phenylsilyl)nickel(II) and bis(1,3-diisopropylimidazol-2-ylidene)hydrido(methyl-(diphenyl)silyl)nickel(II),[47] whereas the *trans* configuration is much more prevalent,[33] for example in the dihalides mentioned above.[43] The bond lengths (Ni–C = 1.865(4) Å, Ni–O = 1.926(3) Å) and bond angles (C–Ni–C = 91.9(2)°, O–Ni–O = 89.80(19)°, C–Ni–O = 89.15(17)°, 178.41(15)°) are within expectations. The two ylides are twisted by 88.58(15)° with respect to each other which allows them to occupy *cis* coordination sites and the ethyl groups are out of the plane of the imidazolylidene rings (C2–N–C–C = 117.2(6)°).

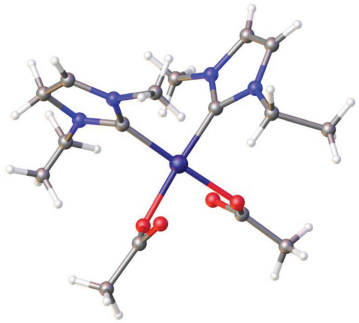


Fig. 8 View of the crystal of bis-(1-ethyl-3-methylimidazol-2-ylidene)-diacetato-nickel(II).

Conclusions

In this paper, the dissolution of the metal oxides Ag_2O, NiO, CuO and ZnO has been investigated in several imidazolium ionic liquids without an additional solvent or additional base. It was found that carbene formation is the driving force behind the dissolution process. New crystal structures of silver(I) and nickel(II) N-heterocyclic carbenes were determined. The speciation of the metal center was investigated by Raman and ^{13}C NMR spectroscopy. Stable zinc(II) carbenes were identified in these ionic liquids. The structure of the ionic liquid is of prime importance for the dissolution process: this means that dissolution was only found for imidazolium ionic liquids with a hydrogen atom in the C2 position of the imidazolium ring, because only these ionic liquids can form carbenes by deprotonation of the C2 carbon. Neither in imidazolium ionic liquids with a methyl group in the C2 position nor for ionic liquids with cations other than imidazolium, dissolution of metal oxides was observed. The anion also plays a role, since carbene formation was observed for imidazolium ionic liquids with chloride, thiocyanate, dicyanamide and acetate anions, but not for bis(trifluoromethylsulfonyl)imide anions.

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CHAPTER

7

CONCLUSIONS & FUTURE PERSPECTIVES

7.1 Conclusions

Due to their advantageous characteristics and unique coordination environment, ionic liquids offer specific potential as solvents for solvent extraction processes and the dissolution of metal oxides. Whereas the potential use of ionic liquids in these applications has been investigated in the past, some problems have been reported. In solvent extraction, there is the well-known ion-exchange problem by which metal ions are exchanged with the constituent parts of the ionic liquid. In the dissolution of metal oxides, the issue for ionic liquids as media to dissolve metal oxides had been associated with the digestion of the strongly bonded O^{2-} anion.

In this work different approaches have been presented in an attempt to overcome the practical problems of ion exchange. We have offered a greener approach to solvent extraction by replacing volatile organic compounds with non-volatile ionic liquids. For the processing of metal oxides in ionic liquids, another approach has been used by adding an oxide-binding agent such as acids to the ionic liquid solution.

Additionally, the speciation of the metal ions in solution and the reaction of metal oxides in ionic liquids has been investigated.

The first part of this PhD dissertation presented the use of the ionic liquid trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101) as extraction phase for the extraction and separation of metal ions from chloride media. The selective extraction of cobalt from nickel to Cyphos®IL 101 was demonstrated and a separation factor of about $5 \cdot 10^4$ was achieved. Cobalt was extracted to the ionic liquid phase as the tetrachlorocobaltate(II) complex, leaving behind the positively charged nickel complex in the aqueous phase. After extraction, cobalt could easily be stripped using water and the ionic liquid was recycled for reuse. An advantage associated with the use of an ionic liquid extraction process was that volatile and odorous compounds were eliminated and that it offered a more sustainable approach to solvent extraction leading to environment-friendlier and healthier working conditions. Furthermore, the practical issues accompanied with ion exchange are solved in this case – extracting cobalt as the anionic chloro complex to the chloride-based ionic liquid, there is no net loss of the ionic liquid constitutes to the aqueous phase. It was reported that the extraction efficiency was affected by the cobalt concentration in ionic liquid phase upon extraction of cobalt, influencing both the viscosity and the distribution coefficient of cobalt. This implied that cobalt loadings of less than 20 g L^{-1} should be used, but starting feeds with high cobalt content can be handled by increasing the volume ratio. Furthermore, the separation with sodium chloride as chloride source was demonstrated, yielding a good separation. An extraction test involving other metals namely manganese, cobalt, magnesium, calcium and nickel demonstrated that manganese was co-extracted with cobalt while the others were remained in the aqueous phase. Three other phosphonium and one ammonium ionic liquids, namely trihexyl(tetradecyl)phosphonium bromide (Cyphos® IL 102), tetraoctylphosphonium bromide (Cyphos® IL 166), tributyl(tetradecyl)phosphonium chloride (Cyphos® IL 167), and methyltrioctylammonium chloride (Aliquat® 336) were compared for their extraction capabilities and it was shown that the alkyl chains of the cation affects the extraction efficiency. Trihexyl(tetradecyl)phosphonium chloride showed to be the best option as ionic liquid phase as a compromise between commercial availability, separation characteristics and the ease to handle the ionic liquid.

This ionic liquid separation process was then conducted in a lab pilot-scale continuous process and the setup with one extraction step, a washing step and three counter-current stripping steps gave pure cobalt (> 99.8%) and nickel (> 99.5%) streams. After the stripping steps, the ionic liquid phase was regenerated. This process showed that ionic liquids can be implemented in industrially applied solvent extraction processes and that in spite of the high viscosity, the ionic liquid phase was able to function in a continuous process. This was possible because the

viscosity drastically dropped upon saturation with aqueous solution and heating. It was shown that this process can be made competitive with the current industrially applied processes after applying minor optimizations.

The second part showed the used of a water saturated acidic solution of Cyphos® IL 101 to dissolve metal oxides (CaO, MnO, Fe_2O_3, CoO, NiO, CuO and ZnO) directly in ionic liquid phase. This presented particular opportunities for bringing metal ions which cannot enter the ionic liquid phase via extraction into ionic liquid solution. It offered opportunities to further process these metals in ionic liquid phase. Selection of an ionic liquid which was not soluble in water makes the process viable on the long term, water as a reaction product can be discharged without loss of ionic liquid. Therefore the hydrophobic ionic liquid Cyphos® IL 101 was selected. Additionally, the mutual separation by back-extraction of the dissolved metals namely calcium, manganese, iron, cobalt, nickel, copper and zinc using Cyphos® IL 101 as extraction phase was investigated. It was shown that nickel and calcium could be separated from cobalt, manganese, and copper, zinc and iron. But the mutual separation between cobalt, manganese, copper and iron proved to be difficult. Recovery of the ionic liquid was possible by changing the stripping conditions and the ionic liquid could be reused after removal of iron, zinc and copper by washing with an ammonia solution. Copper and zinc formed ammine complexes and were back-extracted, while iron precipitated as iron(III) hydroxide, Cyphos® IL 101 proved to be stable upon mixing with the ammonia solution. After removal of all the metals present in the ionic liquid phase, the ionic liquid could be reused.

In the third part the proof-of-principle of the separation of metals by solvent extraction using two mutually immiscible ionic liquids has been shown. Cobalt was extracted from the ionic liquid 1-ethyl-3-methylimidazolium chloride to the ionic liquid trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate and a distribution ratio of 44 was obtained. Cobalt could be selectively separated from nickel and a separation factor of about 200 was achieved. The stripping of cobalt from the hydrophobic phosphonium ionic liquid phase, followed by regeneration of the ionic liquid for reuse, was demonstrated. Although the proposed ionometallurgical process could offer the advantage of a different extraction mechanism and other selectivities, The disadvantage was that there is little space left for tuning the selectivity within a particular system. This in contrast with extraction from aqueous solutions where parameters such as electrolyte concentration or pH can be varied to tune the extraction selectivity for one particular metal.

The last part showed the dissolution of metal oxides in several imidazolium ionic liquids. The crystal structure of the product that crystallised from an ionic liquid containing dissolved Ag_2O showed that this was a silver(I) carbene complex. The speciation of the metal center was investigated by Raman and ^{13}C NMR spectroscopy. Carbene formation was observed for chloride, thiocyanate, dicyanamide and acetate anions, but not for bis(trifluoromethylsulfonyl)imide anions, this implied that the

anion played a role in the reaction mechanism too. Furthermore, the dissolution of other metal oxides (CuO, ZnO and NiO) in 1-ethyl-3-methylimidazolium acetate and chloride was studied. Stable zinc carbenes were identified in the ionic liquids by ^{13}C NMR spectroscopy, but the formation of crystal structures could not be obtained. The solutions formed by dissolution of CuO and NiO in the imidazolium ionic liquids could not be investigated by ^{13}C NMR, because of their paramagnetic behaviour. In a related study a new crystal structure of an nickel(II) carbene complex was found starting from a solution of nickel(II) chloride dissolved in a mixture of 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium acetate.

7.2 Future Perspectives

Aqueous chemistry is an enormously powerful tool for the refining of metals due to its adaptability to new matrices, the low cost and the enormous data of metal species in solution at all conditions. These features make it very suitable for the refining of metals. A substantial shift towards ionometallurgy, in which aqueous solutions are replaced by ionic liquids, is therefore inconceivable. However, within existing hydrometallurgic systems such as solvent extraction, ionic liquids do have specific potential: the replacement of organic solvents by ionic liquids can increase the metal loading in the extraction phase and lead to a clean technology.

The example for the separation of cobalt and nickel, in which Cyphos® IL 101 was used as an extraction medium, showed that this process is promising. Nevertheless, before ionic liquids can be applied in real industrial processes there are still elements that need further consideration. Losses of the extraction phase are inherent to solvent extraction[1] and so far, there is no literature on the aqueous solubility of the cations Cyphos® IL 101 and similar ionic liquids. Therefore, the chemical solubility of these cations at different process conditions needs to be known. Also, one must be aware that high viscosities, inherent in ionic liquid technology, can require process modifications.

Cyphos® IL 101 and similar ionic liquids have potential in many other extraction processes in which anionic metallate complexes can be selectively extracted from metals which will not be present in this form. It is well known that platinum group metals (PGMs) are processed from a chloride medium after leaching with hydrochloric acid with added chlorine. Here as well, Cyphos® IL 101 could have potential as an extraction medium for the separation of the PGMs. However, it is not essential to process metals from chloride media; other types of starting feeds can be used too. By replacing chlorides with nitrates for instance, opportunities are offered to selectively extract lanthanides from a concentrated aqueous nitrate solution, since trivalent rare-earth ions can form anionic complexes with bidentate

nitrate ligands, whereas most other elements cannot. This can be relevant to rare earth recycling.[2]

The industrial implementation of the cobalt-nickel separation by two mutually immiscible ionic liquids is unlikely to happen in the near future, given the facts of a relatively low separation factor and the poor tunability compared with the current state of the art. However, one can think of other applications in which the proposed concept of the mutually immiscible ionic liquids can have specific potential for the separation of metals. This is in cases where non-aqueous technologies are beneficial compared to traditional aqueous separation technologies, such as the reprocessing of spent nuclear fuel. The main purpose of the reprocessing of spent fuel is the separation of the residual uranium and newly formed plutonium from fission products and higher actinides. Ionic liquids are less efficient moderators than water and have therefore already been proposed as possible alternatives for the aqueous phase in the PUREX process.[3] The concept of metal extraction between two mutually immiscible ionic liquids can exclude water and hence prevent the solution from becoming supercritical. The selection of other mutually immiscible systems, which containing other anionic components than the one proposed, can allow control of the speciation of metal solutes to further increase the selectivity for the metal of interest.

The application of ionic liquids as solvents for the leaching of minerals and metal oxides is an other interesting area. The green advantages for ionic liquids will come from the avoidance of producing large volumes of dilute aqueous waste containing heavy metals.[4] It could be questioned whether ionic liquids will ever replace current traditional leaching processes. This will only be the case if ionic liquids lead to a significant improvement, such as other selectivities than those obtained from aqueous solutions; or if processing from ionic liquids has exceptional advantages, such as circumventing oxide and hydroxide products during processing. Furthermore, ionic liquid recycling should be possible given their higher price. Until now, only very little work had been done on this subject. Further investigations will be necessary to obtain a more comprehensive understanding of the metal speciation, the mechanism of the reaction and the effect of additional reagents.

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APPENDIX

A

SUPPLEMENTARY INFORMATION OF CHAPTER 5

A.1 Supplementary ^{1}H NMR data

Solubility of [C_2mim]Cl in the [P_{66614}][R_2POO] phase:

The [P_{66614}][R_2POO] phase was analyzed by ^{1}H NMR. By comparing the phosphonium multiplet (8H) at 2.4-2.5 ppm with the imidazolium peak at 11.6 ppm (1H), the solubility of [C_2mim]Cl in the upper phase ([P_{66614}][R_2POO]) was determined (Figure A.1).

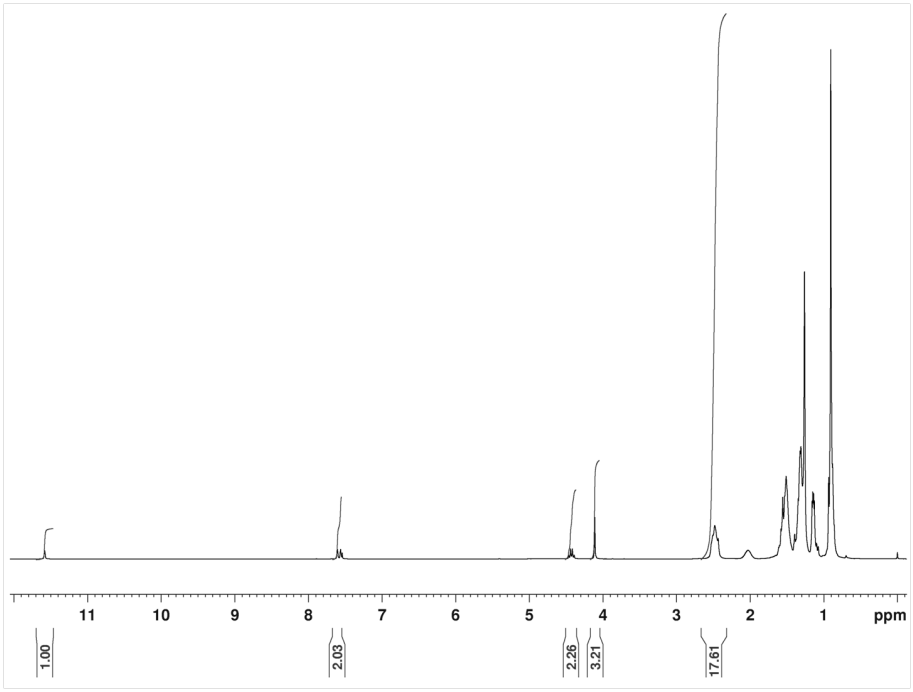

Figure A.1: ^{1}H NMR spectrum of [P_{66614}][R_2POO] after mixing with the [C_2mim]Cl phase

Solubility of [P_{66614}][R_2POO] in the [C_2mim]Cl phase:

The [C_2mim]Cl phase was analyzed by ^{1}H NMR. By comparing the phosphonium multiplet (8H) at 2.4-2.5 ppm with the imidazolium peaks at 10.5 ppm (1H), it was tried to quantify the [P_{66614}] cation concentration in [C_2mim]Cl (Figure A.2). The integration values are too low to obtain reliable data for the solubility. However only measuring the solubility of the cation is not sufficient since anions can exchange with each other as well, where phosphinate anions then replaces chlorides. The peaks due to the methyl groups on the branched alkyl chains of the phosphinate anion situated in the ^{1}H NMR spectra at 0.89 can be detected. The solubility of about 1000 ppm was found. Since the process is used for extraction of cobalt, which has a high affinity for phosphinate ligands, after mixing the phases the phosphinate concentration is expected to be even lower.

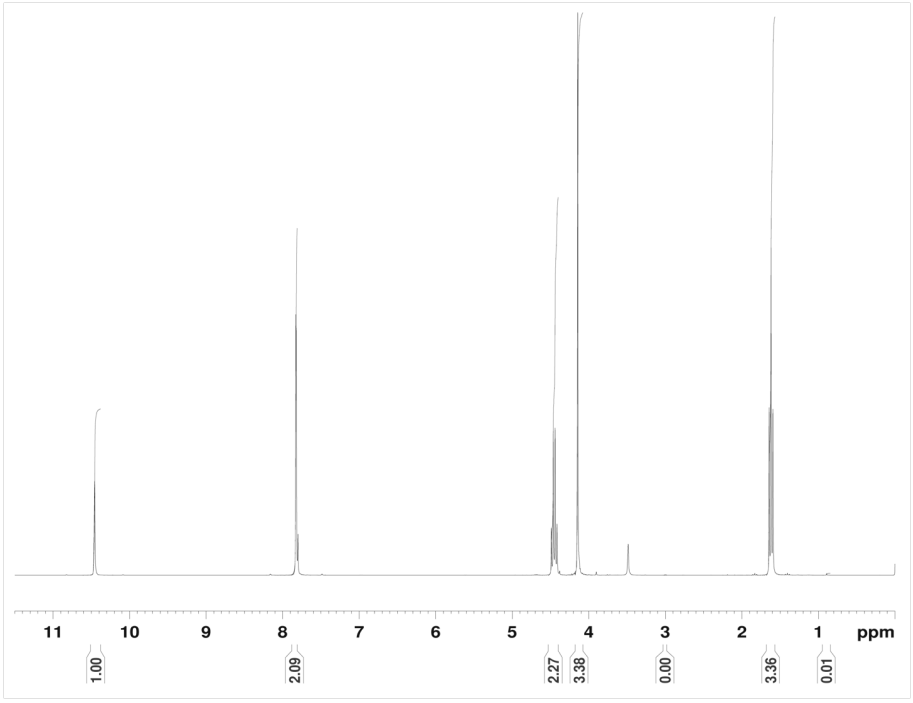

Figure A.2: ^{1}H NMR spectrum of the [C_2mim]Cl phase after mixing with [P_{66614}][R_2POO]

Solubility of [C_2mim]Cl in [P_{66614}][R_2POO] after the washing step:

To quantify the concentration of [C_2mim]Cl in the [P_{66614}][R_2POO] phase after the washing step, a ^{1}H NMR spectrum of the extraction phase was recorded. By comparing the phosphonium multiplet (8H) at 2.4–2.5 ppm with the imidazolium peak at 11.6 ppm (1H), the solubility of [C_2mim]Cl in [P_{66614}][R_2POO] was determined (Figure A.3).

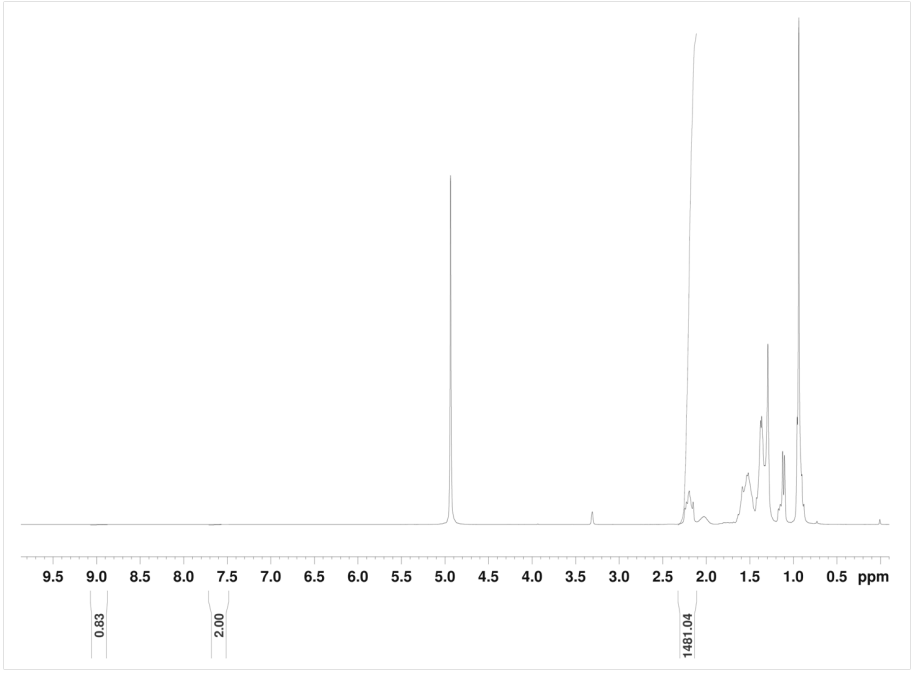

Figure A.3: ^{1}H NMR spectrum of [P_{66614}][R_2POO] after washing

Temperature dependence of the solubility of phosphinate anions and cobalt(II) phosphinate complexes in [C_2mim]Cl:

It was observed that the distribution ratio for cobalt decreased as a function of temperature (see Figure 3 in main text). This behavior can be explained by the increase in solubility of the phosphinate anion in the ionic liquid [C_2mim]Cl with temperature. The solubility of $[R_2POO]^-$ in [C_2mim]Cl was quantified at 140 °C, by ^{1}H NMR measurement after bringing the two ionic liquids in contact by stirring their mixture for 10 minutes (Figure A.4).

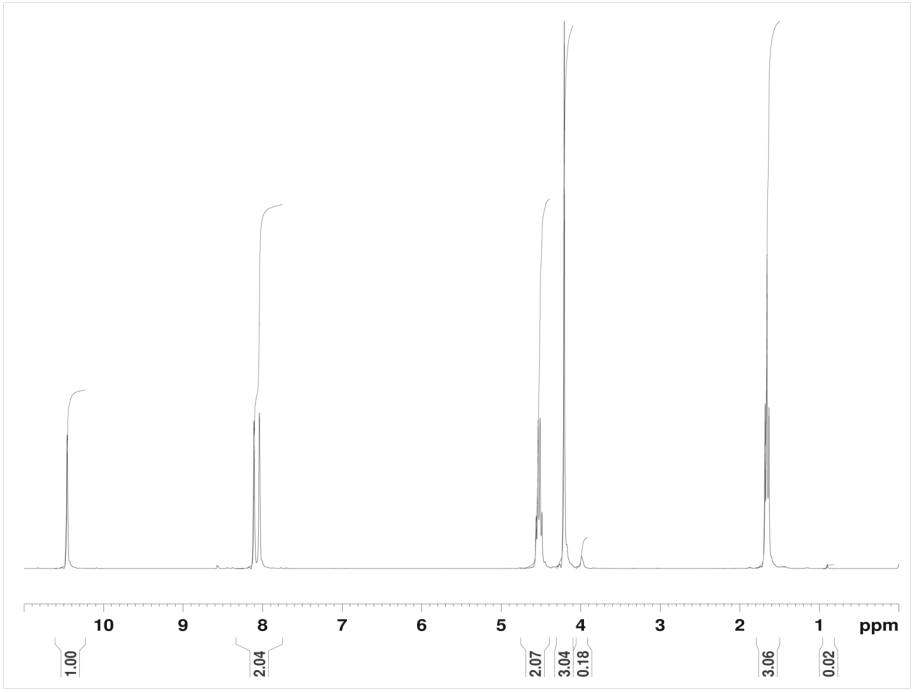

Figure A.4: ^{1}H NMR spectrum of [C_2mim]Cl after extraction at 140 °C

A.2 UV-Vis absorption spectra

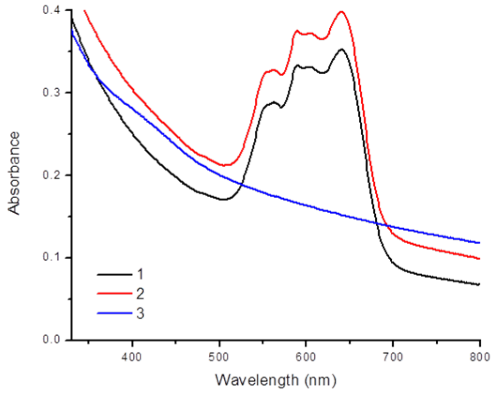

Figure A.5: Absorption spectra of cobalt(II) and nickel(II) in the $[P_{66614}][R_2POO]$ phase after extraction. With spectrum 1 corresponding to cobalt in $[P_{66614}][R_2POO]$ after extraction; 2 to cobalt and nickel in $[P_{66614}][R_2POO]$ after extraction; and 3 to nickel in $[P_{66614}][R_2POO]$ after extraction.

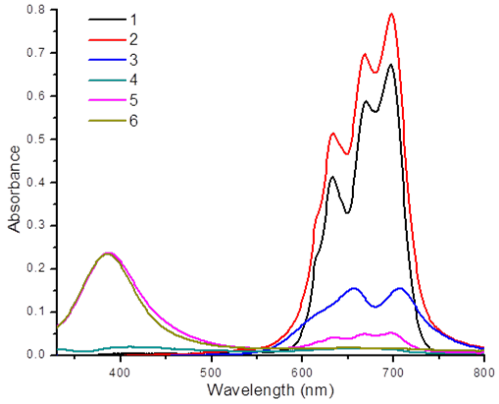

Figure A.6: Absorption spectra of cobalt(II) and nickel(II) in the $[C_2mimCl]$ phase before and after extraction. With spectrum 1 corresponding to $CoCl_2$ in $[C_2mim]Cl$ before extraction; 2 to $CoCl_2$ and $NiCl_2$ in $[C_2mim]Cl$ before extraction; 3 to $NiCl_2$ in $[C_2mim]Cl$ before extraction; 4 to cobalt in $[C_2mim]Cl$ after extraction; 5 to cobalt and nickel in $[C_2mim]Cl$ after extraction; and 6 to nickel in $[C_2mim]Cl$ after extraction.

A.3 Supplementary ^{31}P NMR data

To prove the phosphonium cation and phosphinate anion to be still present in a 1:1 ratio after the processing steps, ^{31}P NMR measurements were measured after each step. The ratio between was checked by integration of the phosphonium peak at 38.1 ppm (1P) and phosphinate peak at 43.6 ppm (1P) in the ^{31}P NMR spectra, during the processing steps, which are extraction, washing and recovery. For the stripping step, the ratio between the peaks at 38.1 ppm (1P) and at 54.11 ppm (1P) in the ^{31}P NMR spectra was determined. The latter peak originates from the formation of the phosphinic acid in acidic medium. If the peaks are integrated, it can be noticed that more phosphinic acid is present. This is explained by taking into account the impurity of phosphinic acid, which was already present in the ionic liquid before the extraction.

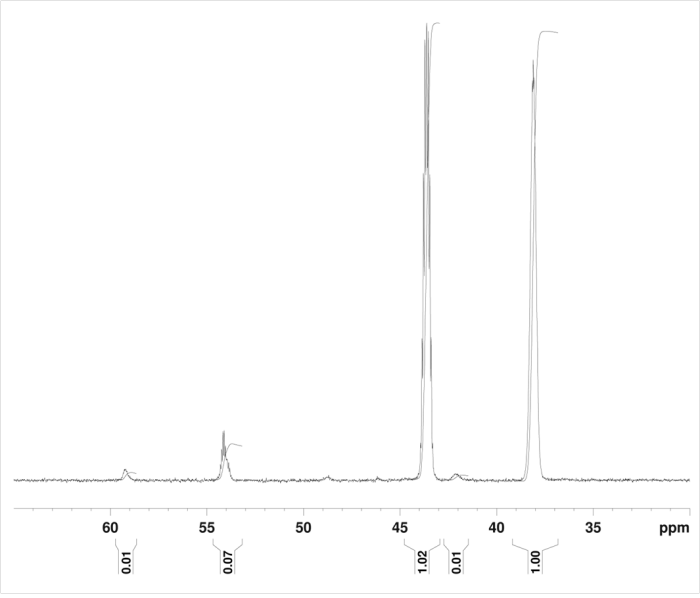

Figure A.7: ^{31}P NMR spectrum of $[P_{66614}][R_2POO]$

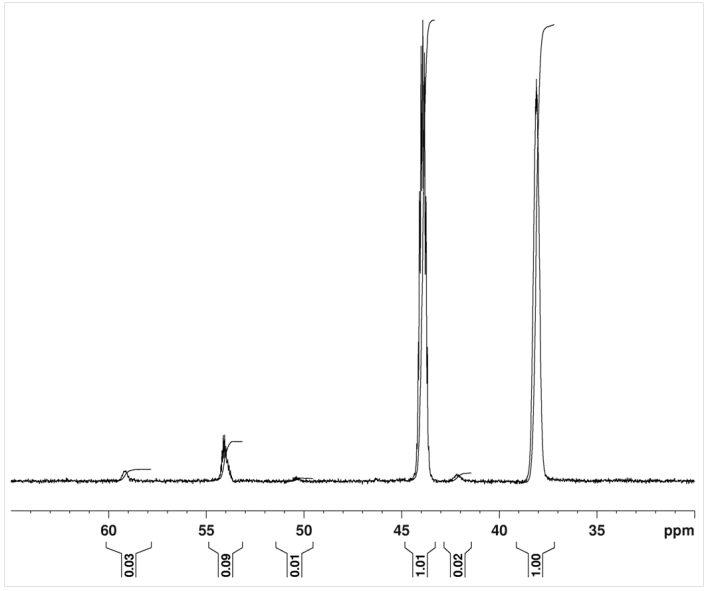

Figure A.8: ^{31}P NMR spectrum of $[P_{66614}][R_2POO]$ after extraction

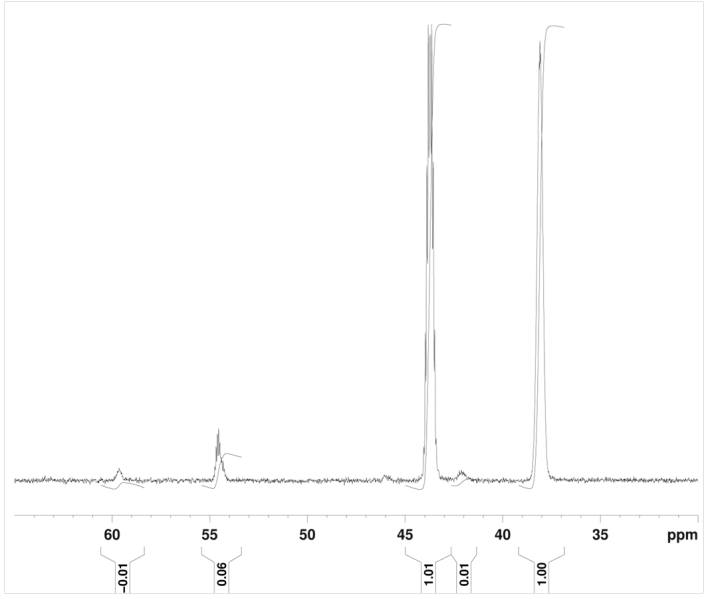

Figure A.9: ^{31}P NMR spectrum of $[P_{66614}][R_2POO]$ after recovery

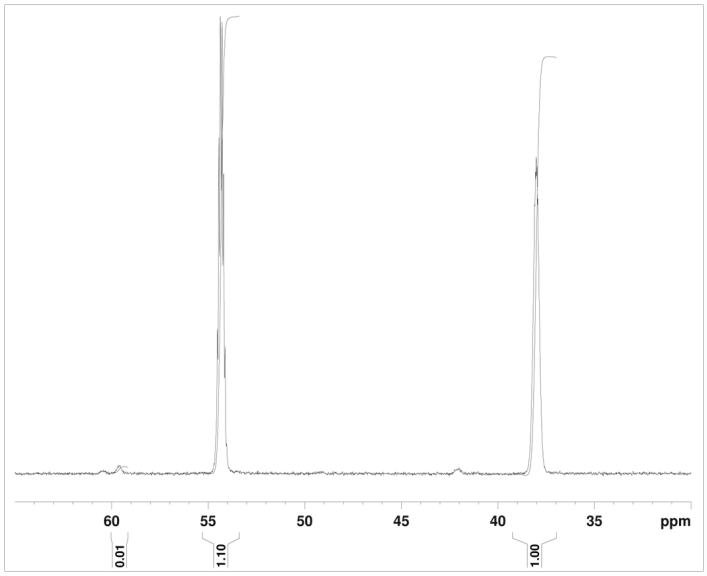

Figure A.10: ^{31}P NMR spectrum of $[P_{66614}][R_2POO]$ after stripping

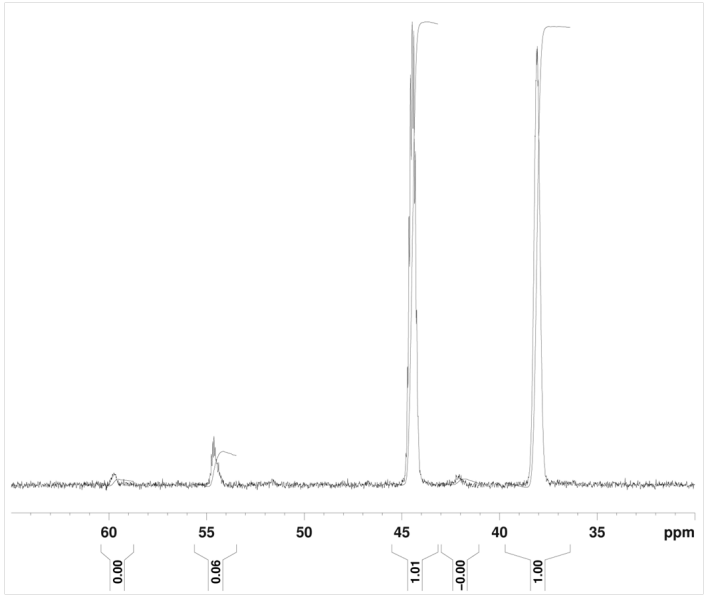

Figure A.11: ^{31}P NMR spectrum of $[P_{66614}][R_2POO]$ after washing

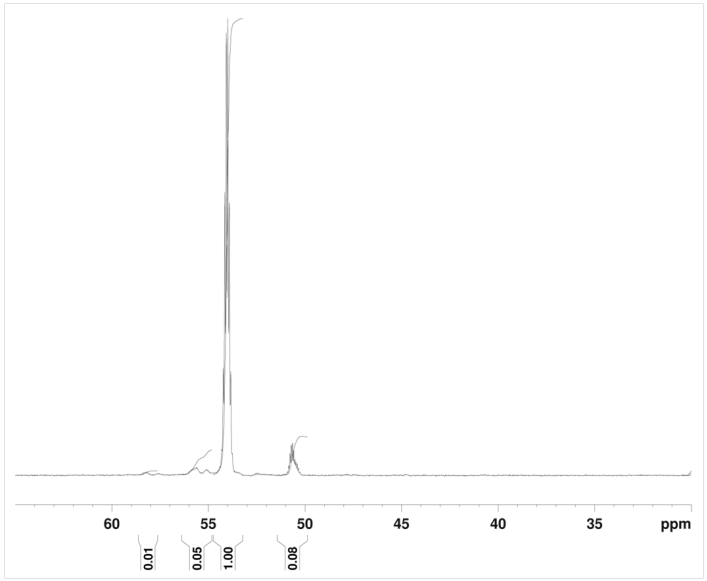

Figure A.12: ^{31}P NMR spectrum of Cyanex272

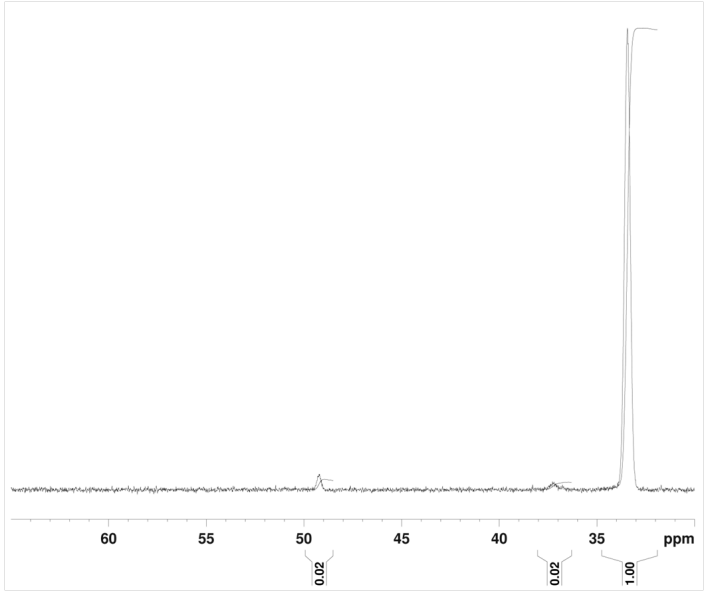

Figure A.13: ^{31}P NMR spectrum of $P_{66614}Cl$

APPENDIX

B

SAFETY ASPECTS

The experimental work performed during this thesis was executed in compliance with the code of practice for safety in the lab,[1] and the departmental safety brochure.[2] Specific caution is necessary for working with E4 products with clearance and hazardous lab equipment (such as bromine). Specific information for personal protection and precautions can be found at departmental website.[3] Cobalt and nickel are carcinogenic suspicious and can cause genetic defects and allergic symptoms; it may damage fertility. Although ionic liquids are often generalized as 'green solvents' based on their negligible vapor pressure at room temperature, one has to be cautious with this postulate and it is of prime importance to evaluate the safety of each individual ionic liquid before use. In a letter to the editor an accident was described in which the protic ionic liquid, pyrrolidinium nitrate, exploded while drying it under reduced pressure at 110 °C (vide infra).[4]

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http://chem.kuleuven.be/en/hse/procedures/liab1.htm.

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[4] S. Wellens, B. Thijs, K. Binnemans, *How safe are ionic liquids? Explosion of pyrrolidinium nitrate*, Green Chem., **2013**, 15, 3484-3485.

Green Chemistry

RSC Publishing

LETTER

How safe are protic ionic liquids? Explosion of pyrrolidinium nitrate

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www.rsc.org/greenchem

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A batch of the protic ionic liquid pyrrolidinium nitrate exploded while drying it under reduced pressure at 110 °C, using a rotary evaporator with an oil bath.

Ionic liquids are often considered as safe alternatives for volatile organic solvents, because of their extremely low vapor pressure and their very high flash point.[1] Although ionic liquids can be designed to be energetic materials or even explosives,[2,3] these solvents are in general difficult to ignite. *Protic ionic liquids* (PILs) are a special class of ionic liquids that are formed by the reaction with a nitrogen base and a Brønsted acid.[4] The proton of the Brønsted acid is transferred to the nitrogen atom of the base and an ionic compound is formed, provided that the Brønsted acid is sufficiently strong. A typical example is ethylammonium nitrate (EAN) that is formed by the reaction between ethylamine and nitric acid.[5] Protic ionic liquids are a popular class of ionic liquids because of their easy synthesis and because they are good model systems for physical studies. Several papers on protic ionic liquids have been published in Green Chemistry.[6–9] As part of our ongoing research on the dissolution of metal oxides in ionic liquids,[10] we decided to investigate protic ionic liquids as reactive solvents for metal oxides. A series of different protic ionic liquids was prepared, including pyrrolidinium ionic liquids with different coordinating anions ($[HCOO]^-$, $[HSO_4]^-$, $[NO_3]^-$, $[H_2PO_4]^-$). These pyrrolidinium ionic liquids were first reported by Anouti *et al.*[11] Two different synthetic procedures were described in this reference, one for ionic liquids with organic anions and one for inorganic anions. The difference in the two procedures is primarily the drying step. In the case of ionic liquids with an organic anion, the residual pyrrolidine or acid was evaporated under reduced pressure and the remaining liquid was further dried at 80 °C under reduced pressure (1–5 mmHg). In the case of ionic liquids with inorganic anions, water was removed by addition of 1,2-dichloroethane, followed by azeotropic distillation. After removal of 1,2-dichloroethane, the remaining ionic liquid was dried under vacuum. However, we decided to prepare pyrrolidinium nitrate [Pyrr][NO_3] *via* the method described for the ionic liquids with the organic anions, to avoid the use of carcinogenic 1,2-dichloroethane (Fig. 1). The drying method was slightly modified with respect to the literature method, in the sense that the drying step was performed at 110 °C, instead of 80 °C. The experimental procedure we used was as follows: nitric acid (65% in water) (1 mol, 63.02 g) was added dropwise to pyrrolidine (1 mol, 71.12 g) in a round-bottom flask (250 mL) using a dropping funnel, while being stirred in an ice bath. After stirring at room temperature for 4 hours, the remaining pyrrolidine, water and nitric acid were removed on a rotary evaporator under reduced pressure (16 mbar) at 70 °C. Heating of the flask on the rotary evaporator was done by means of a hot silicon oil bath. Not all of the water could be distilled off, and the temperature was increased stepwise to 110 °C. Suddenly an explosion occurred. The glass round-bottom flask was scattered and part of the hot silicon oil in the heating bath was blasted by the shock to the walls and ceiling in the neighborhood of the rotary evaporator. At the same time, a cloud of reddish-brown nitrogen dioxide gas was visible. Luckily, nobody was injured and there was only material damage.

The explosion can be attributed to the strong oxidizing properties of concentrated nitric acid under the anhydrous conditions, resulting in a violent oxidative decomposition of the organic compounds. A search of the literature revealed that mixing of nitric acid with secondary amines like pyrrolidine has been reported to cause violent reactions. Clark described secondary and tertiary amines as hypergolic with nitric acid.[12]

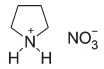

Fig. 1 Structure of the protic ionic liquid pyrrolidinium nitrate.

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More recently, Smiglak *et al.* studied the possibility of forming simple energetic ionic liquids *via* the straightforward protonation of heterocyclic amines and they studied the decomposition mechanism by accelerating rate calorimetry (ARC).[13] The authors found that 1-methylimidazolium nitrate, obtained by mixing of 1-methylimidazole with nitric acid, is a very energetic material. Ethylammonium nitrate has been claimed to be a liquid monopropellant.[14] On the other hand, non-protic ionic liquids with nitrate anions are much less reactive. Schneider *et al.* found no noticeable reactivity of these ionic liquids towards fuming nitric acid.[15]

This incident shows that drying of nitrate protic ionic liquids can be very hazardous. This is important to realize, given the popularity of protic ionic liquids such as ethylammonium nitrate. It is recommended not to heat these ionic liquids above 80 °C, but one has to be aware of the fact that there could be safety issues with protic nitrate ionic liquids even at lower temperatures. Vacuum freeze-drying is suggested as a safer alternative to heating in a vacuum for drying of these protic ionic liquids.[16]

Although many studies have been devoted in the recent years to the toxicity of ionic liquids, the chemical hazards of these solvents are still much less investigated.[17,18] We hope that this letter to the Editor will lead to an increased awareness of the potential dangers of heating protic nitrate ionic liquids.

Notes and references

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Sil Wellens, *A greener approach to hydrometallurgy: highly selective separation of cobalt from nickel by solvent extraction with undiluted phosphonium ionic liquids*, Molten Salts and Ionic Liquids XXIV (Euchem2012), Celtic Manor (Newport, Wales, UK), **5-10 August 2012**, oral presentation.

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